

Technical aspects of production and analysis of biodiesel from used cooking oil—A review

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ARTICLE INFO

Article history:

Received 8 January 2009

Accepted 9 June 2009

Keywords:

Used cooking oil

Transesterification

Biodiesel

Analytical methods

ABSTRACT

The increasing awareness of the depletion of fossil fuel resources and the environmental benefits of biodiesel fuel has made it more attractive in recent times. The cost of biodiesel, however, is the major hurdle to its commercialization in comparison to petroleum-based diesel fuel. The high cost is primarily due to the raw material, mostly neat vegetable oil. Used cooking oil is one of the economical sources for biodiesel production. However, the products formed during frying, can affect the transesterification reaction and the biodiesel properties. This paper attempts to review various technological methods of biodiesel production from used cooking oil. The analytical methods for high quality biodiesel fuel from used cooking oil like GC, TLC, HPLC, GPC and TGA have also been summarized in this paper. In addition, the specifications provided by different countries are presented. The fuel properties of biodiesel fuel from used cooking oil were also reviewed and compared with those of conventional diesel fuel.

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1. Introduction

1.1. Background

Energy use is the most fundamental requirement for human existence. It is indeed the livewire of industrial, food and agricultural production, the fuel for transportation as well as for the generation of electricity in conventional thermal power plants. A high percentage of the world's total energy output is generated from fossil fuels and it has been universally conceded that fossil fuels are finite. The world is no longer endowed with new sources of cheap fossil fuels and experts have warned about the depletion of the present sources in the near future. Furthermore, the threat of supply instabilities and the increased public awareness on the impacts of fossil fuel emissions on the environment and their potential health hazards triggered governments around the world to impose restrictions on fossil fuel combustion emissions [1]. These have simulated interest in alternative sources for fossil fuels especially petroleum-based. One of the most promising sources is biomass [2,3]. Among the biomass sources, vegetable oils and animal fats have attracted much attention as a potential resource for production of an alternative for petroleum-based diesel fuel. This alternative diesel fuel is termed biodiesel. This fuel is biodegradable and non-toxic and has low emission profiles as compared to petroleum diesel [4].

A major criticism often leveled against bio-fuels, particularly against large-scale fuel production, is that it could divert agricultural production away from crops, especially in developing countries [5]. The basic argument is that energy-crop programs compete with food crops in a number of ways and thus could cause food shortages and price increase. This criticism was re-enacted recently following the rise in cost of food items around the world. As a result of this and the potential benefit in the reduction of liquid waste and the subsequent burden of sewage treatment, this study concentrates on the review of various methods of production of biodiesel from used cooking oils (UCOs).

1.2. Vegetable oils as engine fuels

During the World Exhibition in Paris in 1900, Rudolf Diesel tested vegetable oil for his compression ignition engine [6]. However, with the advent of cheap petroleum, appropriate crude fractions were refined to serve as fuel and diesel fuels and diesel engines evolved together [7].

In the 1930s and 1940s, vegetable oils were used as diesel substitutes from time to time, but usually only in emergency situations. Recently, because of increases in the price of crude oil, limited resources of fossil oil and environmental concerns, there has been a renewed focus on vegetable oils and animal fats to make biodiesel.

Vegetable oils occupy a prominent position in the development of alternative fuels although, there have been many problems associated with using it directly in diesel engines especially in direct injection engine [4,7–9]. These problems are associated with large triglyceride molecule and its higher molecular mass can be

solved, if the vegetable oils are chemically modified to biodiesel, which is similar in characteristics to diesel [9,10].

1.3. Biodiesel

The unprocessed vegetable oil can be used in diesel engines, but with required engine adjustments and modifications. Unlike diesel fuel, vegetable oil consists mostly of saturated hydrocarbons and those of vegetable oils are triglycerides, consisting of glycerol and esters of fatty acids. The fatty acids vary in their carbon chain length and in the number of double bonds. To overcome these problems the neat vegetable oils have to be modified to bring their combustion-related properties closer to those of petroleum diesel.

The modifications that have been used include micro-emulsion, pyrolysis (thermal cracking) and transesterification. Among these, transesterification is the key and foremost important step to produce the cleaner and environmentally safe fuel from vegetable oil [4].

Biodiesel is the name given to a clean burning mono-alkyl ester-based oxygenated fuel made derived from natural, renewable feedstock such as new/used vegetable oils, and animal fats. The resulting biodiesel is quite similar to conventional diesel in its main characteristics and can be blended in any proportion with petroleum diesel to create a stable biodiesel blend [8].

2. Biodiesel production

2.1. Transesterification reaction

Transesterification, also known as alcoholysis is the reaction of vegetable oil or fat with an alcohol to form esters and glycerol. To complete a transesterification reaction, stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is needed. In practice, to have a maximum ester yield, this ratio needs to be higher than the stoichiometric ratio. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side [7,8]. The reaction can be catalyzed by alkalis, acids, or enzymes. The reaction is shown in Fig. 1.

Transesterification consists of a sequence of three consecutive reversible reactions. The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and finally monoglycerides to glycerol, yielding one ester molecule for each glyceride at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acids esters and glycerol. The mechanism and kinetics

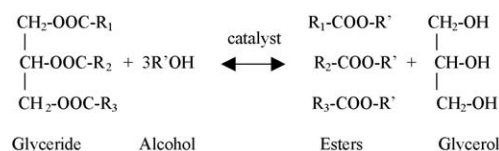


Fig. 1. Transesterification of triglycerides with alcohols.

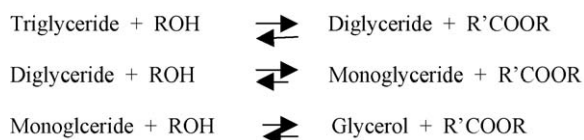


Fig. 2. General equation for transesterification of triglyceride.

of transesterification have been described in detail by [4,7,11]. The basic mechanism is shown in Fig. 2.

2.2. Biodiesel production from used cooking oil

In most parts of the world edible oils are used in frying pans or fryers and after a variable time of use are discarded. These used frying oils have different properties from those of refined and crude vegetable oils. The presence of heat and water accelerates the hydrolysis of triglycerides and increases the content of free fatty acids (FFA) in the oil [12]. The FFA and water content have significant effects on the transesterification reaction negatively [13]. They also interfere with the separation of fatty acid esters and glycerol. Especially, the viscosity of the oil increases considerably, because of the formation of dimeric and polymeric acids and glycerides in used cooking oils. Molecular mass and iodine values decrease while saponification value and density increase [12,14–16].

At present there is no systematic method of processing used oils from households and most of the used oil is mostly thrown through the home drains and ends up in wastewaters that are then discharged to surface waters, leading to water pollution. Moreover, more than 80% of the oil is consumed at home; the control of this disposal behavior becomes a huge problem because of the large volumes involved [17].

Despite the gains made in biodiesel production techniques, the cost of biodiesel is still higher than petroleum-based diesel and this has been a major barrier to its commercialization. One of the ways widely accepted for reducing the cost focuses on minimizing the raw material cost. The use of waste cooking oil instead of virgin (neat) oil to produce biodiesel has been found to be an effective way to reduce the raw material cost. Hence reusing of the waste cooking oil has both the benefit of producing an environmentally benign fuel and solving the problem of waste oil disposal.

The methods of production of biodiesel from used cooking oil do not differ from the conventional transesterification process using alkaline, acidic, and enzymatic catalysts. Depending on the undesirable compounds (especially FFA and water), each catalyst has its advantages and disadvantages. The following section reviews the transesterification methods that have been used for waste cooking oil. A typical schematic diagram for the production of biodiesel from used cooking oil is shown in Fig. 3.

2.2.1. Alkali-catalyzed transesterification

The use of alkali catalysts in the transesterification of used cooking oil is somewhat limited because the FFA in used cooking oil reacts with the most common alkaline catalysts (NaOH, KOH, and CH_3ONa) and forms soap. Because water makes the reaction partially change to saponification, the alkali catalyst is consumed in producing soap and reduces catalyst efficiency. The soap causes an increase in viscosity, formation of gels which reduces ester yield and makes the separation of glycerol difficult. These two problems notwithstanding, literature is replete with studies on the transesterification of waste cooking oil using alkaline catalyst.

NaOH has been used by many researchers for the transesterification of used cooking oil despite its slower reaction rate [15]. Arquiza et al. [18] transesterified with methanol and NaOH as catalyst, used coconut oil with FFA content (% lauric) of 1.47 which greatly exceeded the standard maximum permissible value of 0.07% (lauric) for edible coconut oil. The effects of the following factors were investigated: (1) reaction temperature (30, 45–50 and 60–65 °C); (2) amount of methanol (stoichiometric amount, two and three times the stoichiometric amounts); and (3) catalyst (NaOH) concentration based on the weight of oil (0.1%, 0.5% and 1.0%). It was observed that the yield obtained was the percentage of the maximum amount (in moles) of methyl esters that can be produced. Highest yields of 94% were obtained for the 60–65 °C reaction temperature range, 0.5% catalyst concentration, and twice the stoichiometric amount of methanol. Similarly, the transesterification of used cooking oil with an acid value in the range of 0.42–2.07 mg KOH/g, using NaOH as catalyst, has been reported by Felizardo et al. [19]. A series of experiments were performed to study the effect of methanol/used cooking oil molar ratio between 3.6 and 5.4 and NaOH/used cooking oil weight ratios between 0.2% and 1.0%. For oil with an acid value of 0.42, results show that a methanol/oil ratio of 4.8 and a catalyst/oil ratio of 0.6% gave the

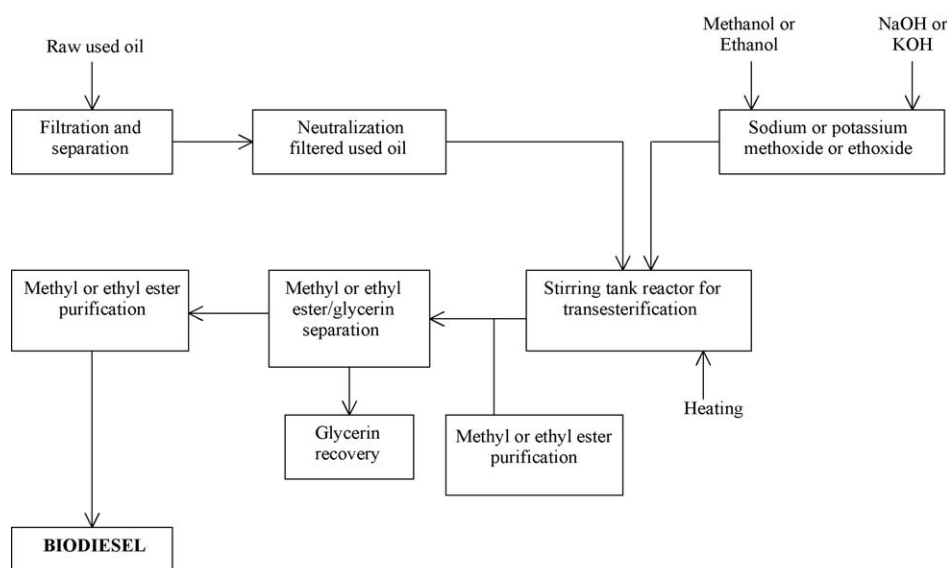


Fig. 3. Schematic flow diagram of the bio-diesel production from used cooking oil.

maximum yield of methyl ester. Recently, Chhetri et al. [20] reported the results of transesterification of used cooking oil with ethanol using NaOH as catalyst. The transesterification was carried out at a reaction temperature of 60 °C and optimum catalyst concentration of 0.08% by weight for 20 min. The average overall conversion achieved was 94.5%. The use of NaOH as catalyst in the transesterification of used cooking oil has also been reported by [21–23].

Tomasevic and Siler-Marinkovic [14] reported the result of transesterification of used sunflower oil (acid value ~ 4) with methanol, using potassium hydroxide (KOH) and sodium hydroxide (NaOH) as catalysts at 4.5:1, 6:1 and 9:1 molar ratios of methanol to oil. Transesterification reaction conditions that affect yield and purity of the product esters such as oil quality, molar ratio of methanol to oil, type and concentration of alkaline catalyst, temperature and reaction time were examined. It was observed that biodiesel of good quality could be obtained from used frying oil in reaction conditions: molar ratio of methanol to oil 6:1, with 1% KOH, temperature at 25 °C and reaction time of 30 min. It was concluded that increase in the quality of a catalyst as well as in molar ratio did not change the yield and the quality of the esters.

Rao et al. [24] prepared fatty acid methyl ester (FAME) by alkali-catalyzed transesterification from used sunflower with low free fatty acids (FFA). The transesterification process was carried out with methanol in the presence of potassium hydroxide (KOH) catalyst. The reaction temperature was 55 °C for duration of 2 h. The process parameters were experimentally optimized but with no details were given in the report. Recently, Reefat et al. [25] reported the results of their studies on the variables affecting the yield and characteristics of biodiesel produced from used cooking oil. The transesterification process was carried out with KOH and NaOH as catalysts at two concentrations (0.5% and 1.0% w/w), two reaction temperatures (25 and 65 °C) and three methanol/oil molar ratios (3:1, 6:1 and 9:1). Higher yields of biodiesel were reported with KOH. The results showed that the best yield percentage was obtained using methanol/oil molar ratio of 6:1, KOH as catalyst (1% concentration) and temperature of 65 °C. Using the same type of catalyst (KOH), the transesterification of used cooking oil with acid values of samples ranging from 0.67 to 3.64 mg KOH/g and saponification values from 264 to 272 mg KOH/g was performed with methanol [26]. The effects of methanol/oil molar ratio, KOH concentration and temperature on the biodiesel conversion were investigated. The results showed that the highest yield of biodiesel (88–90%) was obtained at the ratio of methanol/oil of 7.8–8.1 during 80–90 min at temperatures ranging from 30 to 50 °C in the presence of 0.75 wt% KOH catalyst. In investigating the effect of KOH-to-UCO ratio, ethanol concentration, and time of reaction on the biodiesel yield, Allawzi and Kandah [27] carried out the transesterification of used soybean oil. The reaction was performed at constant temperature of 35 °C in order to minimize the cost of heating and ethanol evaporation. A 2³ complete factorial design on biodiesel yield was performed using low and high levels of operating variables: KOH concentration (9–14 g/l), ethanol concentration (30–40 vol%) and time (30–40 min). The highest yield was obtained in the first 30 min of reaction time. The results indicate that the highest yield was 78.5 vol% using a KOH-to-UCO ratio of 12 g/l and 30 vol% ethanol.

Dorado et al. [28] compared the catalytic activities of NaOH and KOH for the transesterification of waste cooking oil with FFA content of 2.76 and concluded that the KOH transesterification proceeds faster than NaOH-catalyzed reaction. Potassium hydroxide has been considered as a best catalyst for transesterification of used cooking oils [29]. Hence, many researchers have used it for the transesterification of waste cooking oil.

In the above reported cases, NaOH and KOH catalysts performed well, probably due to the very low FFA content in the used cooking

oil. Hence, the problem of saponification was not serious. If the FFA content exceeds 1% and if an alkaline catalyst must be used, then a greater amount of catalyst should be added to neutralize the FFA [15]. Reed et al. [30] described one such method of producing esters from used cooking oil containing significant quantities of FFA liberated during the cooking process. The oil reacted with NaOH dissolved in methanol. The significant difference compared to conventional alkali-catalyzed process is that additional quantity of alkali was used to neutralize the fatty acids in the waste cooking oil plus 0.3% excess prior to transesterification. The transesterification of processed (with citric acid added to remove solids) and unprocessed used cooking oil, was carried out using methanol, and KOH as catalyst and 6:1 methanol/oil molar ratio at room temperature [31]. Excess catalyst was used to neutralize the FFA present in the used cooking oil. The ester yield was 51 wt% with processed UCO and 58 wt% with the unprocessed UCO. Results showed that the properties of the processed UCO and unprocessed UCO did not compare well with the canola and green-seed canola methyl esters (used as control) as the UCO esters had poor lubricity number. Lowe et al. [32] used the same concept to produce hydrogenated soybean ethyl esters (HYSEE) from used French fry oil and ethanol of molar ratio 1:6 in the presence of 1.43% KOH as main treatment catalyst. For each percent of FFA, an excess of 0.197 g of KOH was added. To prevent emulsion in the washing phase, 1-octanol, tannic acid and water were added. The biodiesel conversion obtained was in excess of 92%. Dorado et al. [33] carried out the transesterification of UCO (palm oil and Brazilian hydrogenated fat with 5.12% FFA, Spanish olive oil with 2.24% FFA and a mixture of several other German vegetable oils with 1.28% FFA), using KOH as catalyst. A two-step transesterification process was carried out using a stoichiometric amount of methanol and the necessary amount of KOH and sufficient quantity of KOH to neutralize the FFA. It was concluded that a two-step transesterification process without any costly purification steps is a good method for biodiesel production from UCO of different origins with FFA less than 3%. The conversion efficiency obtained was in the range of 88–95% after the two-step transesterification process. Çayh and Küsefoğlu [34] have reported the results of comparing one-step and two-step base-catalyzed room temperature transesterification reaction of used cooking oil. In the two-step base-catalyzed process, for 1000 g of UCO, 4.2 g NaOH and 140 ml methanol was used in the first step and 1.8 g NaOH and 60 ml methanol was used in the second step. All reactions were carried out at 25 °C; the effects of water content and suspended particles were studied. Results showed that the two-step process is better than the one-step process in terms of lower reaction temperature, reduced catalyst and alcohol used and high yields obtained.

Apart from NaOH and KOH which are the most commonly used alkali catalysts, the use of sodium methoxide (NaOCH₃) and potassium methoxide (KOCH₃) as alkaline catalysts have been studied with sodium methoxide proving to be a better catalyst. Alcantara et al. [17] performed a transesterification process of three fatty acid materials (soybean oil with acid index of 0.53%), UCO (acid index of 0.47%) and tallow (acid index of 6.8%) using sodium methoxide as a catalyst. The optimum conditions reported were: molar ratio of methanol to oil, 7.5:1; reaction temperature, 60 °C; catalyst concentration, 1% NaOCH₃ and stirring speed of 600 rpm. Under these optimized conditions, all the substrates gave a greater than 95% conversion to methyl ester. Although it is widely reported in literature that the performance of alkaline catalysts reduces in the presence of FFA greater than 1%, these researchers reported that the stirring speed was a critical factor not the acidity index of the oil when NaOCH₃ is used as a catalyst. The reusability of this catalyst for the transesterification of new UCO was also reported. It was observed that the reused catalyst showed a slightly longer induction period than the original one but at the end of

Table 1

The properties of the vegetable oil.

Density at 15 °C (kg/m ³)	Viscosity at 40 °C (mm ² /s)	Cetane index	Acid value (mg KOH/g)	Peroxide value (g I ₂ /100 g)	Saponification value (mg KOH/g)	Iodine value value (g I ₂ /100 g)
933	64.1	49.1	3.82	20.2	196	117

Table 2Effect of oil quality on ester properties/molar ratio = 4.5:1; temperature, 60 °C; time, 60 min; catalyst = 9% NaOCH₃.

Density at 15 °C (kg/m ³)	Viscosity at 40 °C (mm ² /s)	Cetane index	Acid value (mg KOH/g)	Peroxide value (g I ₂ /100g)	Saponification value (mg KOH/g)	Iodine value (g I ₂ /100 g)	Yield of crude ester (% on oil basis)
886	5.5	58	0.032	25	196	110	85.5

about 60 min, the conversions for the used and fresh catalysts were similar.

Jordanov et al. [35] used waste cooking oil from sunflower to perform transesterification reaction with sodium methoxide as catalyst. The properties of the vegetable oil used are presented in Table 1 [35]. The reaction conditions were: molar ratio of methanol to oil 4.5:1, KOH concentration of 9%, sodium methoxide concentration 1–10% (v/v), temperature 60 °C and reaction time of 1 h. The results obtained, Table 2 [35] showed that the quality of used frying oil does not have an essential effect on the quality of esters produced if optimal conditions of transesterification process are chosen.

Encinar et al. [29] compared the catalytic activities of NaOH, KOH NaOCH₃ and KOCH₃ in a two-stage transesterification of UCO with methanol that had an FFA content of 1.15%. The study focused on the effects of the following variables: molar ratio of methanol to oil (3:1–9:1), catalyst concentration (0.1–1.5%), temperature (25–65 °C) and catalyst type on the ester yield. Results showed that the biodiesel with the best properties was obtained with a methanol/oil molar ratio of 6:1, KOH as catalyst (1%) and temperature of 65 °C. It was observed that the two-stage process with separation of glycerol after the first stage was better than a one-stage process. These researchers [29] repeated the study using ethanol under the following operation variables: ethanol/oil ratio (6:1–15:1) and temperature (35–78 °C). In this case, biodiesel with the best properties was obtained using molar ratio of 12:1 and temperature of 78 °C. Similar result was obtained (KOH as catalyst, 1%) as in the case of methanol. It was also concluded that the two-stage process was better than the one-stage. The ester yield improved by 30% when compared with one-stage process.

The characteristics and performance of NaOH, KOH and NaOCH₃ on UCO have been evaluated by Leung and Guo [36]. The UCO has an acid value of 2 and viscosity of 35 cSt. The study showed that although NaOH has intermediate catalytic activity and a much lower cost, it was more superior to the other two catalysts. The process variables that influenced the transesterification of triglycerides were investigated and optimized. It was found that the optimal reaction for the process was achieved at 60 °C for a reaction time of 20 min, 1.1 wt% NaOH and 7:1 molar ratio of methanol to oil. However, due to the ease of separation of the ester layer from the glycerol layer, using KOH is more convenient and simpler since the glycerol in the liquid state can be removed easily by direct outflowing from the bottom of the separation unit. For this reason, KOH is commonly used for production of biodiesel from waste recycled oil feedstock. Recently, Dias et al. [37] carried out a study whose objective was to evaluate the biodiesel synthesis from waste cooking oil (acid value, 0.82 mg KOH/g and iodine value, 117 g I₂/100 g), sunflower oil (acid value, 0.08 mg KOH/g and iodine value, 123 g I₂/100 g) and soybean refined oil (acid value, 0.21 mg KOH/g and iodine value, 127 g I₂/100 g), using KOH, NaOH and NaOCH₃ as catalysts. The amounts of catalysts varied from 0.2% to 1% of oil mass for virgin oils and 0.4% to 1.2% of oil

mass for the UCO. Using NaOCH₃ and NaOH, the optimum conditions which ensured that the parameters studied fulfilled the required limits to the European biodiesel standard EN 14214 was 0.8 wt% of UCO. KOH was found to be less effective compared with the sodium-based catalysts. Although 0.8 wt% of KOH for UCO ensures that the viscosity is within the limits, purity was lower than the minimum required according to the standard. Because purity at the highest concentrations of KOH was close to the limit, it was concluded that best results would be expected by increasing the catalyst concentration (greater than 1.2 wt%).

The use of liquid-amine-based catalyst for the transesterification of soybean oil, used cooking oil and tallow has been reported by a group of Spanish researchers [17]. The UCO was originally a mixture (~50% v/v) of olive oil and sunflower oil with acidity index of 0.47. The chemical transformation of triglycerides was accomplished in a single chemical process with the conversion reaching about 75% in less than 40 h. A vacuum distillation step was used to isolate the amide biodiesel from the oil. Cerce et al. [38] screened four amine-based catalysts: diethylamine, diethylethanol amine (DMAE), tetramethyl diaminoethane (TEMED) and tetramethylammonium hydroxide (TMAH), for the transesterification of virgin and used frying oil. The highest conversion of 98% was achieved with TMAH as a catalyst at 65 °C in 90 min. However, this required a large quantity of liquid amine as high as 13% for the reaction. The amines not only act as a solvent for the reactants but also for the products. Therefore, the chemical equilibrium is shifted to the right side and favors more product formation.

Microwave irradiation is a well-established methodology to improve extraction and to accelerate chemical reactions such as those of hydrolysis and esterification [39]. Lertsathapornasuk et al. [40] investigated the effect of using microwave irradiation in the acceleration of conversion of used cooking oil to biodiesel. Transesterification of used vegetable oil was carried out by varying the following parameters: (i) molar ratio of ethanol to oil (3:1, 6:1, 9:1, 12:1, 15:1 and 18:1) and (b) reaction time (10, 20, 40, 50, 60, 80 and 100 s). Sodium hydroxide (1%) was selected as the catalyst. Results indicate that the optimum conditions for complete conversion of the used oil to ethyl ester was 9:1 molar ratio and 1% (w/v) NaOH at 10 s. The reaction time for biodiesel production under microwave irradiation was reduced by more than 10 times. The percentage yields of the esters are shown in Table 3 [40]. Similarly, Saifuddin and Chua [41] carried out transesterification process to investigate the effect of microwave irradiation on the biodiesel production. Two-step transesterification reaction with UCO and anhydrous ethanol (6:1 molar ratio to oil) which represented a 100% excess of the stoichiometric amount required and 0.5% NaOH was used as catalyst. The reaction was performed at room temperature and six reaction mixtures were prepared and allowed to react for 3, 15, 30, 45, 60 and 75 min, respectively. The reaction was arrested in each sample by adding 10–15 drops of water. To investigate the effect of microwave irradiation, the oil and ethanol were heated at 60 °C using

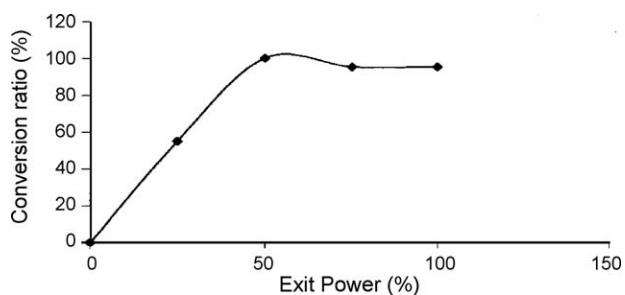
Table 3

Yield percentages of fatty acid ethyl esters from used cooking oil.

Reaction time (s)	% yields of fatty acid ethyl ester at molar ratio					
	3:1	6:1	9:1	12:1	15:1	18:1
10	7.19%	23.90%	100%	100%	100%	100%
20	5.44%	34.27%	100%	100%	100%	100%
30	3.82%	27.84%	100%	100%	100%	100%
40	5.93%	31.32%	100%	100%	100%	100%
50	6.69%	39.21%	100%	100%	100%	100%
60	6.67%	32.31%	100%	100%	100%	100%
80	2.52%	41.16%	100%	100%	100%	100%
100	8.67%	24.87%	100%	100%	100%	100%

microwave oven. The reaction mixture was irradiated using 25% of an exit power of 750 W. Five sets of the reaction mixtures were prepared and allowed to react for 1, 2, 3, 4 and 5 min respectively. To arrest the reaction, similar quantities of drops of water were added. Experiments were repeated for 50%, 75% and 100% exit power of 750 W for all the five different reaction time. The results of the conventional and microwave-assisted process were compared. It was observed that the microwave irradiation of the reaction mixture inside a microwave oven greatly reduced the time required to achieve maximum conversion. Fig. 4 shows a power level of 50% of an exit power of 750 W was required to achieve maximum conversion [41]. While the conventional process requires 75 min, the microwave-assisted process took only 4 min.

The methods of continuous preparation of fatty acid ethyl esters from coconut, rice bran and used frying (palm) oils in a modified home-made microwave oven (800 W) have been investigated by Lertsathapornasuk et al. [42]. Good yields of fatty acid ethyl esters were obtained with 1.0% NaOH (in excess) as a catalyst. With the alcohol to oil molar ratio of 9:1, 100% conversion was obtained within 30 s for coconut oil, 94% conversion for rice bran oil and 83% conversion for used frying oil. Percent conversion was slightly increased for UCO but not for rice bran oil, when the reaction time was increased to 60 s. The temperatures of the reaction mixtures were rapidly increased to the boiling point of alcohol within 30 s and increased slightly above the boiling point of the alcohol, to 83.4 °C at 60 s. When the used frying oil was thinned with kerosene (1:1 v/v), percent conversion was 92% in 30 s, which is slightly higher than the un-thinned oil. Percent conversions remained constant at longer reaction times. Reaction temperature was lower than the un-thinned oil (70.9 °C at 30 s and 80.2 °C at 60 s). The percent conversion of triglycerides to fatty acid ethyl ester is given in Table 4 [42]. Recently, the same researchers [43] modified the process and used it to carry out the transesterification of waste frying palm oil (WFPO). The WFPO contained very high FFA (4.50%). The FFA was not removed but was neutralized with NaOH in situ. Thus, NaOH concentration in ethanol was increased to 3.0%. Part of the NaOH was used for neutralization and the remainder acted as transesterification catalyst. With the ethanol to oil molar ratio of 12:1 and residence time of 30 s, the continuous conversion of

**Fig. 4.** Effect of microwave power level on transesterification of used cooking oil.**Table 4**

Percent conversion of triglycerides to fatty acid ethyl ester.

Sample	Reaction time (s)	Reaction temperature (°C)	Conversion (%)		
			Fatty acid ethyl ester	Triglyceride	Free fatty acid
^a Used palm oil			0	95.5	4.5
Used palm oil	30	77.5	82.5	10.7	6.8
Ethyl ester	45	81.2	83.9	9.4	6.7
	60	84.1	90.6	2.7	6.7

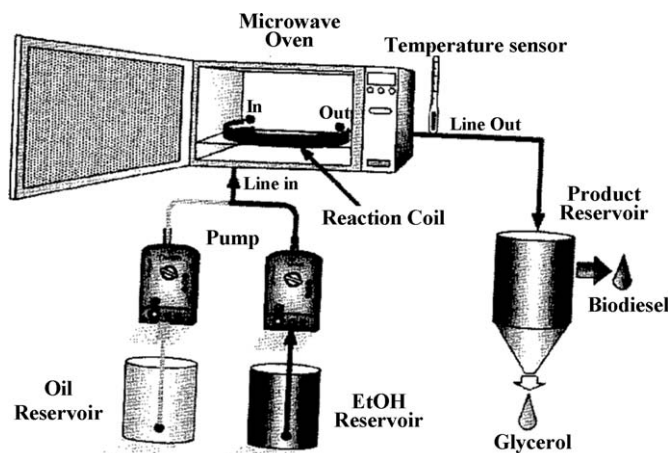
^a Starting material compositions.

WFPO to ethyl ester was over 97%. The energy consumption of this process was about 74.8 Wh/l. The schematic diagram of the continuous microwave biodiesel reactor is shown in Fig. 5 [43].

Similarly, Reefat et al. [44] reported the use of microwave irradiation in the production of biodiesel. The optimum parametric conditions obtained from the conventional technique [25] were applied using microwave irradiation in order to compare both systems. The results showed that application of radio frequency microwave energy offers a fast, easy route to biodiesel production with advantages of enhancing the reaction rate and improving the separation process. From these results it was concluded that using microwave irradiation reduces the reaction time by 97% and the separation time by 94%.

2.2.2. Pretreatment of used cooking oil before alkali-catalyzed transesterification

Analysis shows that the differences between UCO and virgin oils are not very great [45]. Therefore, in most cases, heating and removal by filtration of solid particles suffices for subsequent transesterification. However, in some cases the products of oil decomposition cause deterioration in oil quality, which can lead to

**Fig. 5.** The schematic diagram of the continuous microwave biodiesel reactor.

reduced ester yield during biodiesel production and the formation of unwanted products. The negative effects of the undesirable compounds can be avoided by treatment of the used cooking oil. Different types of pretreatment have been used for the purification of UCO prior to alkali transesterification. These include: steam injection, column chromatography, neutralization, film vacuum evaporation and vacuum filtration [15].

Supple et al. [46] used steam and sedimentation method to investigate the effects of oil pretreatment on the properties of UCO and the esters produced from it. The study was carried out in two stages consisting of pretreatment and heating of the oil at 65 °C, followed by sedimentation in both stages. The effects of these treatments on the physical and chemical properties of UCO are shown in Table 5 [46]. Results after both stages of pretreatment show that there was a reduction in moisture content, free fatty acid and a substantial reduction in viscosity while the calorific value increased. The pretreated UCO was transesterified with methanol (6:1 molar ratio) using 1% KOH as the catalyst at 60 °C. The decrease in FFA (6.3–4.3%) and moisture content (1.4–0.4%), respectively accounted for the substantial increase in ester yield (from 67.5% to 83.5%) observed.

The effects of pretreatment of UCO on ester yield by column chromatography were studied by Ki-Teak and Foglia [47]. Used cooking oil containing 10.6% FFA and 0.2% water was purified by passing it through 50% aluminum oxide. The FFA and water contents decreased from 10.6% to 0.23% and from 0.2% to 0.02 wt%, respectively. The conversion of untreated UCO before column chromatography was observed to have increased from 25% after 24 h of reaction, to 96% when pretreated oil was used.

Cvengros and Cvengrova [48] used a sequence of pretreatment methods to reduce the FFA, water, and polymer content in UCO before carrying out a two-stage transesterification with KOH as catalyst at 65 °C for 90 min. FFA was removed by neutralization with alkalis (KOH or NaOH) and removed as soaps while high polymer content was treated with activated carbon and removed by adsorption. Film vacuum evaporation was found to be more suitable for de-acidification and drying. While drying was performed under moderate conditions of 159 °C and 20 mbar, de-acidification required more severe conditions of 200–280 °C and 0.1–8 mbar. The reported yield of methyl ester obtained from the treated oil was 96%.

Other pretreatment methods have been reported in literature: filtration and drying using microwave oven at 60 °C for 10 min [41]; drying over magnesium sulfate and subsequent filtration under vacuum to remove any suspended matter and magnesium crystals [19]. Prior to transesterification of UCO using alkali catalyst, Issariyakul et al. [49] carried out pretreatment by centrifuge to remove solid portion of the oil. Water was removed by mixing UCO with 10 wt% silica gel (28–200 mesh) followed by stirring and vacuum filtration. Recently, in their study, Dias et al.

[37] filtered UCO under vacuum after dehydration over night using anhydrous sulfate, and finally filtered again under vacuum prior to transesterification. To produce biodiesel from used frying sunflower oil, Predojevic [50] pretreated the oil by drying over calcium chloride and filtered through cellulose filter to remove any suspended matter and calcium chloride crystals.

One limitation to the alkali-catalyzed process using KOH and NaOH is their sensitivity to the purity of the reaction; the alkali-catalyzed system is very sensitive to both water and FFA [51,52]. The presence of water may cause ester saponification under alkaline conditions. Also, FFA can react with an alkali catalyst to produce soaps and water. Saponification not only consumes the alkali catalyst, but also the resulting soaps can cause the formation of emulsions. Emulsion formation creates difficulties in downstream recovery and purification of the biodiesel. Thus, dehydrated vegetable oil with FFA not greater than 1%, an anhydrous alkali catalyst and anhydrous alcohol are necessary for commercially viable alkali-catalyzed systems. In the alternative, additional alkaline catalyst is required to neutralize the FFA. These requirements are likely to affect the cost of the biodiesel. The amount of liquid amine catalyst required (13%) for the transesterification is very high. Also, the efficiency of the conversion (75% in less than 40 h) needs to approach quantitative values if the amide biodiesel is to be of any economic interest since the lengthy vacuum distillation step used to remove this catalyst would raise the overall operating cost. Although the removal of impurities such as water, FFA, and polymers prior to alkali-catalyzed transesterification can improve the yield and quality of the esters from UCO, it would increase the cost of pretreatment, leading to increases in the cost of biodiesel. The mechanism of microwave effect on a chemical reaction, whether thermal or non-thermal is debatable. Again, if irradiation times and radiation power levels are not properly controlled, it will result in deterioration of both biodiesel yield and purity.

2.2.3. Acid-catalyzed transesterification

As previously stated, one limitation of alkali-catalyzed transesterification is due to the sensitivity this process has to the purity of the reactants, especially to water and FFA. Freedman et al. [53] have reported that acid catalysts are insensitive to FFA and are better than the alkaline catalysts for vegetable oils with FFA greater than 1%.

The transesterification of edible oil using strong acids are available in literature reports [54–57]. Transesterification of triglycerides is catalyzed by inorganic acids such as sulfuric acid, hydrochloric acid, phosphoric acid and sulfonated organic acids. Acid-catalyzed transesterification starts by mixing the oil directly with the acidified alcohol, so that separation and transesterification occur in single step, with the alcohol acting both as a solvent and as esterification reagent [58].

The transesterification of UCO from cafeterias using sulfuric acid and KOH was compared by Nye et al. [59]. Partially hydrogenated

Table 5
Effects of various treatments on the physical and chemical properties of used cooking oil.

Property	Batch 1			Batch 2		
	Raw	T1 ^a	T2 ^b	Raw	T1	T2
Moisture content (%)	1.1	0.5	0.4	1.4	0.6	0.4
Density (kg/m ³)	0.937	0.925	0.921	0.93	0.929	0.922
Kinematic viscosity (mm ² /s)	190.2	130.1	85.3	201.3	110.2	70.1
Acid value	5.3	4.4	3.9	6.3	4.9	4.3
Iodine value	104.3	103.7	105.2	115.3	117.2	116.2
Peroxide value (meq/kg)	5.6	5.3	4.6	6.3	5.7	4.4
Saponification number	204.3	194.2	184.2	195.1	194.3	193.9
Unsaponifiable matter (%w/w)	3.9	2.7	1.9	4.9	3.0	2.1
Energy value (kJ/g)	37.2	38.8	38.6	37.9	38.3	39.1

^a First stage of pretreatment and heating at 65 °C, followed by sedimentation.

^b Second stage of pretreatment and heating at 65 °C, followed by sedimentation.

Table 6

Reaction conditions for transesterification of used oils and yields of fuels.

Alcohol	Molar ratio (alcohol:oil)	Temperature (°C)	Time (h)	Catalyst	Ester yield (wt%)	
					2 days at 25 °C	7 days at 25 °C
Methanol	3.6:1	65	40	0.1% H ₂ SO ₄	79.3	64.0
Methanol		50	24	0.4% KOH	91.9	85.3
Ethanol	3.6:1	73	40	0.1% H ₂ SO ₄	66.9	54.8
Ethanol		50	24	0.4% KOH	28.9	
1-propanol	3.5:1	90	40	0.1% H ₂ SO ₄	92.2	76.2
1-propanol		50	24	0.4% KOH	42.7	
2-propanol	3.5:1	80	40	0.1% H ₂ SO ₄	78.7	54.4
2-propanol		50	24	0.4% KOH	51.2	
1-butanol	3.6:1	105	40	0.1% H ₂ SO ₄	78.1	61.9
1-butanol		50	24	0.4% KOH	59.5	
2-ethoxyethanol	4.2:1	125	40	0.1% H ₂ SO ₄	53.5	39.2
2-ethoxyethanol		50	24	0.4% KOH	37.0	

soybean oil and margarine were transesterified with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-ethoxyethanol. The ester yields were calculated when the product was allowed to settle for 48 h at 25 °C, followed by the removal of solids by gravity and filtration. The filtrate was then allowed to stand at 5 °C for 7 days and re-filtered. Results showed that acid-catalyzed esters had higher yields, compared to the alkali-catalyzed reaction, except for methyl esters although the process took a longer time. The reaction conditions and results are given in Table 6 [59].

Ripmeester [60] and McBride [61] conducted pilot-scale transesterification reactions of UCO with excess of methanol in the presence of sulfuric acid catalyst at 70 °C. A minimum molar ratio of 50:1 methanol to oil and acid concentration of 1.5–3.5 mol% (based on reaction mixture) were used. Such a high proportion of methanol was used to promote high equilibrium conversions of oil to esters. Zhang et al. [51] reported obtaining results at 80 °C for the same process. The reaction was carried out in a 15 liter stainless steel reactor equipped with a heating jacket, at a 50:1 molar ratio of methanol to oil, pressure from 170 to 180 kPa and an agitation speed of 400 rpm. Under these conditions, a 97% oil conversion to fatty acid methyl ester was reached within 6 h. An empirical first-order model was proposed and a rate constant was calculated. In continuation of the same study, the researchers [62] showed that the acid-catalyzed transesterification reaction of oil in methanol is essentially a pseudo-first-order reaction provided that the methanol: oil molar ratio is close to 250:1 at 70 °C or in the range of 74:1–250:1 at 80 °C. The results also indicate that under these conditions, quantitative yields of FAME (99 ± 1%) can be obtained at both 70 and 80 °C and at a stirring speed of 400 rpm, using a feed molar ratio oil: methanol: acid of 1:245:3.8 at 70 and 80 °C.

The catalytic activities of various acids for the transesterification of UCO have been compared. Al-Widyan and Al-Shyoukh [63] studied the transesterification of waste palm oil under different conditions. Sulfuric acid and different concentrations of hydrochloric acid and ethanol at different excess levels were used. Using higher catalyst concentrations in the range of 1.5–2.25 M produced biodiesel with lower specific gravity in a much shorter reaction time than lower concentrations. Compared to HCl, H₂SO₄ was a superior catalyst. The use of excess alcohol effected significant reductions in reaction time required for the acid-catalyzed reaction. Hence, Brönsted acid-catalyzed transesterification requires high catalyst concentration and a higher molar ratio to reduce the reaction time.

Apart from Brönsted acids, Lewis acids have found use in transesterification of vegetable oil. Basu et al. [64] have developed a process to produce esters from feedstock with high FFA content, diglycerides and monoglycerides, using calcium and barium acetates as a catalyst. The optimized ratio of calcium to barium acetate was 3:1. This catalyst does not form soap with FFA,

however, ratios of calcium to barium acetates higher than 3:1 promotes the formation of salts. Other limitations include high temperature (200–250 °C) and high pressure (400–600 psi) required for the reaction. Also, barium compounds are toxic in nature. Potassium hydroxide and a combination of barium and calcium acetate as catalysts for the production of methyl ester from UCO have been compared [65]. Results show that at high temperature and pressure, 0.12% barium acetate and 0.34% calcium acetate catalyst gave an ester yield of 87–94 wt% when the molar ratio of methanol to oil was 0.38 at a reaction time of 2–3 h. At a molar ratio of 0.2–0.28, catalyst concentration 0.01–25% KOH with no heating, the ester yield was 83–92% after 1–2 h.

The preparation of biodiesel from UCO by simultaneous esterification and transesterification using homogeneous Lewis acids based on carboxylic salts of cadmium, manganese, lead and zinc have been developed [15]. Acetates and stearates of calcium, barium, manganese, lead, zinc, cobalt and nickel were tested for their catalytic activity for the transesterification of UCO at a molar ratio of oil to alcohol of 1:12 and a temperature of 200 °C for 200 min. Results showed that stearates performed better than acetates because of better solubility in the oil. The catalyst also showed better performance than the Brönsted acids at lower catalyst concentration and a lower molar ratio of oil to alcohol [66].

Homogeneous acid catalysts have proved to be good for the transesterification of UCO with high FFA. However, it suffers some shortcomings such as high alcohol to FFA ratio (20:1–40:1 molar ratio of alcohol to oil), large quantity of catalyst (5–25%), high catalyst concentration and high temperature. Again, the reaction is relatively slow and the catalyst ends up in the by-products causing serious separation problems.

In recent times, attention on biodiesel research has focused on the use of solid acid catalyst also known as heterogeneous catalysts, for the transesterification of low-grade oils with high FFA content. Sulfonic resins, such as Nafion[®] NR50, sulfated zirconia and tungstated zirconia have sufficient acid site strength to catalyze biodiesel-forming transesterification reactions as efficiently as sulfuric acid [67]. Lotero et al. [68] have reported that the ideal solid acid catalyst for the transesterification of UCO should have characteristics such as an interconnected system of large pores, a moderate to high concentration of strong acid sites, and a hydrophobic surface.

Wang et al. [69] have reported the result of a two-step transesterification process adopted to produce biodiesel from UCO. The UCO had acid value of 75.92 ± 0.036 mg KOH/g. The FFA of the UCO was esterified with methanol catalyzed by ferric sulfate which acted as a solid acid catalyst in the first step, and the triglycerides in UCO were transesterified with methanol catalyzed by KOH in the second step. The results showed that ferric sulfate had a high activity to catalyze the esterification of FFA with methanol. The conversion

rate of FFA reached 97.22% when 2 wt% of ferric sulfate was added to the reaction system containing methanol to triglyceride in 10:1 (mole ratio) composition and reacted at 95 °C for 4 h. The methanol was vacuum evaporated, and transesterification of the remained triglycerides was performed at 65 °C for 1 h in a reaction system containing 1 wt% of KOH and 6:1 mole ratio of methanol to oil. The final product with 97.02% of biodiesel was obtained after the two-step process. This two-step catalyzed process provides a simple and economic method to produce biodiesel from UCO as ferric sulfate is environmentally friendly, easy to separate from the system, more efficient and reusable. Wang et al. [70] compared the conventional acid and the new two-step catalyzed processes for synthesis of biodiesel from UCO. Sulfuric acid was used in the conventional acid catalysis while ferric sulfate was used in the two-step method. The FFA content and the reaction conditions are as in Wang et al. [69]. The conversion of free fatty acids of UCO into FAME in the two-step method was 97.22% at the reaction time of 4 h, mole ratio of methanol to oil of 10:1, compared with the FAME yield of 90%, at reaction time of 10 h, mole ratio of 20:1 obtained in the acid method. It was concluded that the new two-step process showed advantages of no acidic wastewater, high efficiency, low equipment cost, and easy recovery of catalyst when compared with the limitations of acidic effluent, no reusable catalyst and high cost of equipment in the conventional acid process.

Recently, Cao et al. [71] investigated the transesterification of UCO with high acid value and high water contents, using heteropolyacid $H_3PW_{12}O_{40} \cdot 6H_2O$ (PW_{12}) as catalyst. The hexahydrate form of PW_{12} was found to be most promising catalyst which exhibited highest ester yield of 87% for transesterification of UCO and ester yield of 97% for esterification of long-chain palmitic acid respectively. The PW_{12} acid catalyst shows higher activity under the optimized reaction conditions compared with conventional homogeneous catalyst sulfuric acid, and can easily be separated from the products by distillation of the excess methanol and can be reused many times. This most important feature of this catalyst is that the catalytic activity is not affected by the content of free fatty acids and the content of water in UCO. Also transesterification can occur at a lower temperature (65 °C), a lower methanol/oil molar ratio (70:1) and a shorter reaction time. The results show that PW_{12} acid is an excellent water-tolerant and environmentally benign acid catalyst for the preparation of biodiesel from UCO.

Also, in an attempt to develop a robust solid acid catalyst that can simultaneously catalyze esterification as well as transesterification reaction, different types of solid acid catalysts such as MoO_3/SiO_2 , MoO_3/ZrO_2 , $WO_3/SiO_2-Al_2O_3$, zinc stearate supported on silica were synthesized and evaluated for biodiesel production from used cooking oil containing 15 wt% free fatty acids [72]. Zinc stearate immobilized on silica gel (ZS/Si) was found to be the most active and stable heterogeneous catalyst. The catalyst was reused many times without any loss in activity and at the optimized conditions of reaction temperature of 200 °C, stirring speed of 600 rpm, 1:18 molar ratio of oil to alcohol, and 3% (w/w) catalyst loading, a maximum ester content of 98 wt% was obtained.

The advantages of using solid acid catalysts include: (i) they are insensitive to FFA content; (ii) esterification and transesterification can be performed simultaneously; (iii) removal of the catalyst is easy; (iv) the product, fatty acid esters, does not require water washing; (v) ester yields are generally high; (vi) the catalyst requirements per ton of biodiesel are much lower than for other processes; (vii) the catalysts can be used for an extended time; and (viii) they are environmentally friendly. However, these systems operate under high temperature and pressure.

2.2.4. Acid- and alkali-catalyzed two-step transesterification

As previously stated, alkaline and acidic catalysts have their own advantages and disadvantages in the transesterification of used cooking oil. Hence, to avoid the problems associated with the

use of these catalysts separately, especially the problems of saponification and slow reaction time, many researchers have developed the two-stage acid-and-alkali-catalyzed transesterification. In the first stage, esterification of FFA present in UCO is carried out using acid to decrease the FFA level to less than 1%. In the second stage, transesterification of the neutral UCO is performed using an alkaline catalyst.

Lepper and Friesenhagen [73] have patented a two-stage acid/alkali-catalytic process for the production of fatty acid methyl esters of short-chain aliphatic alcohol from fats and/or oil with FFA content greater than 1%. The oil was subjected to esterification with monohydric alcohol in the presence of acidic catalyst (sulfuric, sulfonic acids) at temperature 50–100 °C and pressure ≤ 5 bar in the presence of glycerol or ethylene glycol which served as a liquid entraining agent for the removal of water formed during the acid-catalyzed reaction. This procedure was found to be economical and efficient for the transesterification of UCO with a high content of FFA.

A process has been developed where the high FFA feedstock was initially treated using H_2SO_4 to reduce the FFA to less than 1%. The pretreated feedstock with $<1\%$ FFA was then transesterified with methanol in the presence of KOH catalyst. The effects of alcohol type (methanol or ethanol), the amount of catalyst (0, 5, 15 and 25 wt%) and reaction time (1, 15, 30 and 60 min) on the reduction of FFA level were investigated using several synthetic mixtures of virgin oil as well as yellow grease (12% FFA) and brown grease (33% FFA) [74]. It was concluded that (i) methyl ester yield from UCO improved; (ii) the rate of reaction increased with increase in the amount of acid catalyst; (iii) the acid value of yellow and brown grease decreased to less than 2 mg KOH/g at molar ratio of methanol to FFA (40:1) and reaction time of more than 1 h was required.

Hancsok et al. [75] used the combined acid/alkali-catalyzed transesterification for the production of FAME from UCO (FFA 32.5%, acid value 56 mg KOH/g and iodine value 126 g $I_2/100$ g) and various mixtures of spent frying/neat vegetable oil (FFA 0.5–19 mg KOH/g, acid value 1.039 mg KOH/g and iodine value 115–123 g $I_2/100$ g). Co-solvents such as tetrahydrofuran (THF) and dioxine were employed for increasing inter-phase while H_2SO_4 and sodium methylate were used as catalysts. During the first step, the conditions of the combined transesterification were: temperature, 60 °C; molar ratio of methanol and THF to oil, 4:1; concentration of H_2SO_4 , 15%; reaction time, 0.5–6 h while during the second step the temperature and molar ratio remained the same but 3% sodium methylate catalyst was used in reaction time of 2 h. The experiments were also repeated with dioxine under the same conditions. It was observed that the use of co-solvents significantly reduced the FFA content thereby reducing the reaction time during the first stage, see Figs. 6 and 7 [75]. With the combined transesterification, an ester yield greater than 96.5% was attained.

Transesterification of waste fryer grease (WFG) containing 5–6% (wt%) FFA was carried out with methanol, ethanol, and mixtures of methanol/ethanol maintaining oil to alcohol molar ratio of 1:6, and initially with KOH as a catalyst [49]. Mixtures of methanol and ethanol were used in order to use the better solvent property of ethanol and rapid equilibrium conversion using methanol. Formation of soap by reaction of FFA present in the WFG with KOH led to separation problems between biodiesel and glycerol. To untangle this problem, the two-stage (acid- and alkali-catalyzed) method was used for biodiesel preparation. In the first stage, esterification of FFA present in WFG was carried out using sulfuric acid as a catalyst and in the second stage transesterification of neutral WFG was performed using KOH as a catalyst. Results showed that more than 90% ester was obtained when two-stage method was compared to approximately 50% ester in single stage alkaline catalyst. In the case of mixed alcohol, a small amount of ethyl esters was formed along with methyl esters. The formation of ethyl esters is due to its less reactive intermediate ethoxide.

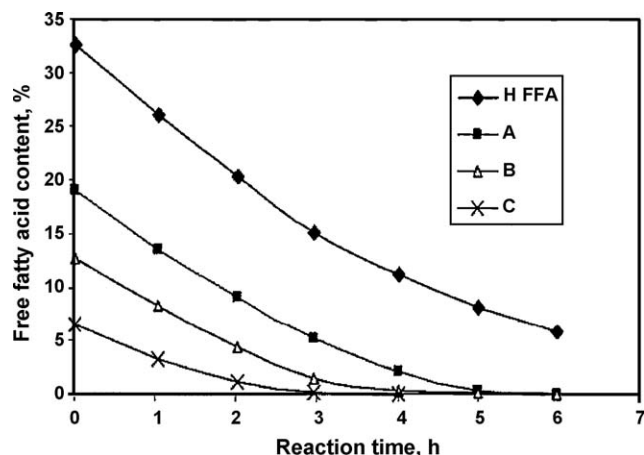


Fig. 6. Change in FFA content during acidic pre-esterification in the absence of co-solvent.

Recently, Meng et al. [76] reported the results of two-stage acid/alkali-catalyzed transesterification performed on waste cooking oil (WCO). The optimum reaction conditions for this process were determined by orthogonal analysis of parameters in a four-factor and three level tests. The optimum experimental conditions obtained from the orthogonal test were: methanol/oil molar ratio of 9:1, 1.0 wt% of NaOH, reaction temperature of 50 °C and reaction time of 90 min. Verified experiments showed methanol/oil molar ratio of 6:1 was more suitable in the process, and under that condition UCO conversion efficiency was 89.8%.

Despite its advantages, the two-stage method also faces the problem of catalyst removal in both stages. The problem of catalyst removal in the first stage can be avoided by neutralizing the acid catalyst, using extra alkaline catalyst in the second stage. However, the use of extra catalyst will increase the cost of biodiesel. Generally, the residue of either alkaline or acidic catalyst in the ester can cause engine problems. Alkaline catalyst can produce higher levels of incombustible ash and acid catalyst attack engine metallic parts. Therefore, the catalysts must always be eliminated from the biodiesel when the reaction is complete [77]. Also, acid or alkali-catalyzed transesterification of UCO has problems such as pretreatment of feedstock, recovery of glycerol, catalyst removal, and the energy-intensive nature of the process that requires high stirring speed and temperature for good conversion.

2.2.5. Enzyme-catalyzed transesterification

In recent times, there has been a growing interest in the use of enzymes such as lipases for catalysis of oils for biodiesel production. Some of the advantages this type of transesterification has over the chemical-catalyzed reactions include the generation

of no by-products, easy product removal, mild reaction conditions (temperature, 35–45 °C), and catalyst recycling [78].

It has been reported that enzymatic reactions are insensitive to FFA and water content in waste cooking oil [15,78,79]. Hence, enzymatic reactions can be used in transesterification of used cooking oil. Nelson et al. [80] screened four lipases: *Mucor Meih* (Lipozyme IM60), *Candida antarctica* (SP435), *Geotrichum candidum* and *Pseudomonas cepacia* (PS30) as catalysts for the transesterification of olive oil, soybean oil, and tallow with short-chain alcohols. The reaction conditions developed for tallow were proved to be effective for transesterification of UCO. The optimized reactions developed were: temperature, 45 °C; stirring speed, 200 rpm; enzyme concentration, 12–25%, and reaction time, 4–8 h (for primary alcohols) and 16 h (for secondary alcohols). *M. Meih* was most effective for the transesterification of tallow using primary alcohols (95% conversion) and *C. antarctica* and *P. cepacia* were most efficient using secondary alcohol (90% conversion).

Sequel to the report that *P. cepacia* was not a good catalyst for transesterification of UCO with primary alcohol, Wu et al. [78] investigated on ways obtaining maximum ester yield from this enzyme. Transesterification of UCO was performed with 95% ethanol. The following optimized conditions (temperature of 38.4 °C, time of 2.47 h, lipase content of 13.12 wt%, and a molar ratio of ethanol to oil of 6.6:1) obtained by factorial design and surface response methodology gave a maximum ester yield of 85 wt%. The addition of 5 wt% supported lipase SP435 from *C. antarctica* after 1 h of reaction with PS-30 increased the ester yield to 96 wt%. The addition of PS-30 lipase in the first step and SP435 in the second step increased the ester yield from 85 to 96 wt%.

The effect of immobilization on the catalytic activity of *P. cepacia* lipase was examined by Hsu et al. [79]. *P. cepacia* lipase (PS-30) was immobilized within a phyllosilicate sol–gel matrix (IM PS-30) and then used for the transesterification of waste fryer grease with primary and secondary alcohols. The reaction was conducted under solvent-free conditions but in the presence of molecular sieves (0.4%), to eliminate water using both free and immobilized PS-30 lipase. The solvent-free condition did not give good conversion with methanol. The process gave poor conversion (47–89%) when free lipase was used. However, immobilized lipase gave better conversions (84–94%) for both primary and secondary alcohols. In the case of ethanol, high ester yields of 81 and 94 wt% were obtained with free and immobilized lipases, respectively. It was also observed that immobilized lipase can be used six times without a significant loss of activity, whereas free lipase lost 50% of its initial activity after second cycle and all activity after the third cycle. Similarly, the performance for the solvent-free transesterification of restaurant grease with a single-step addition of normal alcohols and branched-chained alcohols was compared with that using IM PS-30 by Hsu et al. [80]. Lipases used in this study included *Thermomyces lanuginose* and *C. antarctica* supported on granulated silica (Gran-T.I., and Gran C.a., respectively), *C. antarctica* supported on macroporous acrylic resin (SP435), and *P. cepacia* immobilized with phyllosilicate sol–gel matrix (IM PS-30). The results of ester yields obtained from these fryer greases using different alcohols and enzymes have been tabulated and are shown in Table 7 [15]. The reaction conditions were as follows: molar ratio of grease to alcohol, 1:4; enzyme loading, 10 wt%; reaction temperature, 40 °C; reaction time, 24 h; and no solvent.

Also, Hsu et al. [81] have studied the continuous transesterification of WCO with ethanol using immobilized *Bulkholderias cepacia* (IM BS-30) as a catalyst in a re-circulating packed-column reactor. The effects of feed flow rate (50 ml/min), temperature (40–60 °C), reaction time (8–48 h), and reusability of the enzyme on the product yield was studied. The optimized conditions for 96 wt% ester yields were as follows: feed flow rates, 30 ml/min; temperature, 50 °C; molar ratio of ethanol to grease, 4:1; and

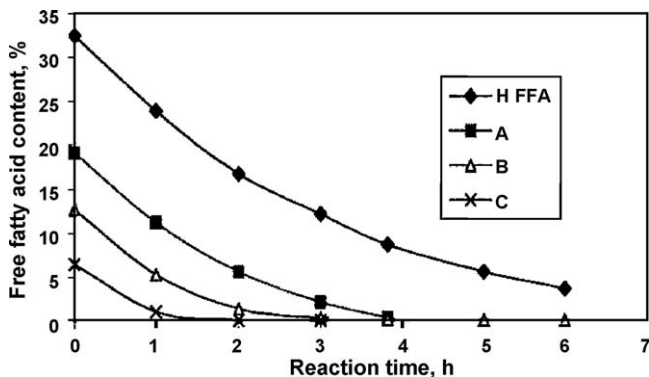


Fig. 7. Change in FFA content during acidic pre-esterification in the presence of THF co-solvent.

Table 7

Yields of esters obtained from restaurant grease using different alcohols and enzymes.

Alcohol	Alkyl ester yield (%)					
	Gran-T.I.	Gran-C.a.	SP435	IM PS-30	free ^a IM PS-30	IM PS 30 ^a
Methanol	4	27	60	88	47	94
Ethanol	87	76	70	88	81	88
Ethanol (95%)	64	41	30	86	81	94
Propanol	87	79	52	87	87	87
2-Propanol	61	59	87	46	75	90
Butanol	90	56	88	97	89	94
Isobutanol	97	89	94	72	87	84

^a Reaction condition: molar ratio of grease to alcohol, 1:4; 100 mg immobilized lipase or 10 mg free lipase powder; reaction temperature, 50 °C; reaction time, 18 h; and 0.4% molecular sieves.

reaction time, 48 h. It was also reported by Nelson et al. [82] that organic-solvent-free methanolysis does not give high conversions. To improve on this process, Watanabe et al. [83] conducted transesterification of UCO via stepwise addition of methanol, which prevented inactivation of the lipase (*C. antartica*). Another advantage of this method is that FFA and water have little or no effect on the efficiency of a stepwise methanolysis and the immobilized biocatalyst can be reused. The transesterification was performed in a three-step flow methanolysis with three fixed-bed bioreactors, a three-step batch methanolysis and a one-step flow methanolysis. Methanol was divided equally for all three steps. 90% of the UCO was converted to the corresponding methyl esters by feeding the substrate mixture into the first, second, and third reactors. It was observed that the products of oxidation and hydrolytic reactions in the UCO did not inhibit the methanolysis of acylglycerols. Similarly, Shimada et al. [84] performed a three-step methanolysis of UCO with lipase. In the process, one-third of the alcohol was fed at the beginning of the reaction, one-third 10 h after the reaction has started and the other third later than 24 h from the beginning of the reaction. A normal graphic obtained is shown in Fig. 8 [84]. Another interesting result is that if the amount of the molar relationship is larger than 0.5, the product becomes insoluble in alcohol. This fact reduces the activation with lipase as shown in Fig. 9 [84].

Nie et al. [85] conducted a three-step transesterification with methanol by using a series of columns packed with immobilized *Candida* species 99–125 lipase. As a substrate in the first step reaction, waste oil (with FFA, 46.75%; monoglycerides, 1.44%; diglyceride, 5.71% and triglycerides, 46.10%) was used together with 1/3 molar equivalent of methanol against total fatty acids in the oil. Mixtures of the first- and second-step eluates and 1/3 molar equivalent of methanol were used for the second- and third-reaction steps. The immobilized lipase had a low temperature optimum and the highest yields were at 40 °C. The final conversion ratio of the

FAME under the optimal conditions was 92%. However, about 15% of water content is important for the conversion ratio of methyl ester. The life of the immobilized lipase was more than 10 days.

Chen et al. [86] investigated enzymatic conversion of waste cooking oils using immobilized lipase based on *Rhizopus oryzae*. The process focused on optimization of several process parameters, including the molar ratio of methanol to WCO, biocatalyst load, and adding method, reaction temperature, and water content. The results indicate that methanol/oil molar ratio of 4:1, immobilized lipase/oil of 30 wt% and 40 °C were suitable under a pressure of 1 atm. Under the optimum conditions the methyl ester yield was around 88–90%. The irreversible inactivation of the lipase is presumed and a stepwise addition of methanol to reduce inactivation of immobilized lipases was proposed.

Thus, immobilization has a substantial effect on the catalytic activity of lipase especially when feedstock with high FFA and water contents is used for the transesterification. Immobilized enzymes such as *P. cepacia* and *B. Cepacia* are efficient enzymes for the transesterification of WCO that is contaminated with FFA and water [15].

Recently, Halim et al. [87] carried out a study aimed at developing an optimal continuous procedure of lipase-catalyzed transesterification of waste cooking palm oil in a packed bed reactor. Response surface method (RSM) based on central composite rotatable design (CCRD) was used to optimize packed bed height and substrate flow rate for the transesterification process. The optimum condition was as follows: 10.53 cm packed bed height and 0.57 ml/min substrate flow rate. The optimum predicted FAME yield was 80.3% and the actual value was 79%.

The advantages of using lipases are [52]:

1. Possibility of regeneration and reuse of the immobilized residue, because it can be left in the reactor if the reactive is kept low;

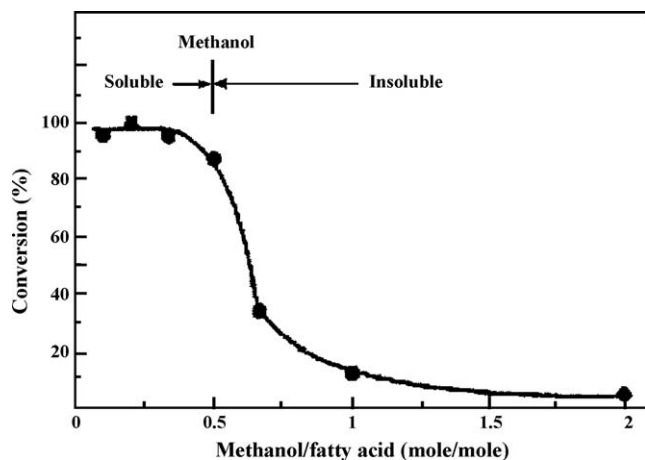
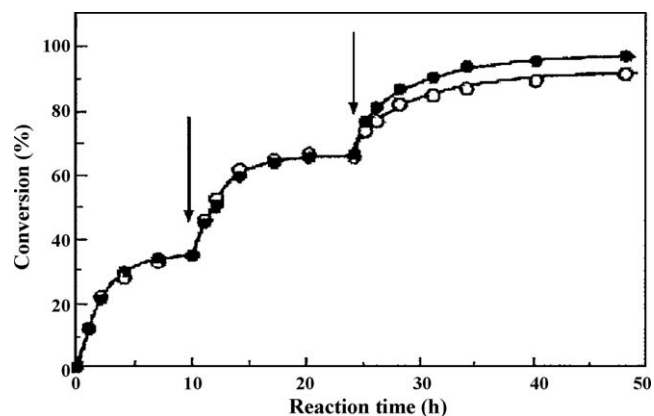


Fig. 8. Three-step batch methanolysis of UCO.

Fig. 9. Methanolysis of vegetable oil with different amounts of methanol using immobilized *C. antartica* lipase.

2. Use of enzymes in reactors allows use of high concentration of them and that makes for longer activation of the lipases;
3. A bigger thermal stability of the enzyme due to the native state;
4. Immobilization of lipase could protect it from the solvent that could be used in the reaction and that will prevent all the enzyme particles getting together;
5. Separation of the product will be easier using this catalyst.

Some disadvantages include:

1. Loss of some initial activity due to the volume of the oil molecule.
2. Number of support enzymes is not uniform.
3. Biocatalyst is more expensive than the natural enzyme.

These advantages notwithstanding, for the use of enzymes, there are some critical factors: there is a minimum water content needed by the lipase, below which it does not function; alcohol has an effect on the reaction, methanol being the most commonly employed; the effect of temperature is significant because instead of increasing the rate of reaction by increasing the temperature, enzymes may become denatured at high temperatures; and since all oils do not have the same amount or type of fatty acids, lipase specificity can become more attractive in some oils than in others [58].

2.2.6. Non-catalytic conversion technique for transesterification

Due to poor methanol and oil miscibility, conversion of oil is a very slow reaction. The non-catalyst options are designed to overcome the reaction initiation lag time caused by this extremely low solubility of the alcohol on the triglyceride phase. One approach that is now commercialized is the use of co-solvent that is soluble in both methanol and oil. The result is a fast reaction, on the order of 5–10 min, and no catalyst residues in either of the ester or the glycerol phase. One of such co-solvents is tetrahydrofuran, chosen in part, because it has a boiling point very close to that of methanol and the system requires a rather low operating temperature of 30 °C. The patented BIOX production process uses this approach to convert both triglycerides and free fatty acids in a two-step, single phase, continuous process at atmospheric pressures and near-ambient temperatures, all in less than 90 min. Through the addition of a co-solvent, the FFAs are first converted and then the triglycerides into methyl esters without any pre-treatment step. The process achieves feedstock conversion of greater than 99% even when using higher FFA feedstock (up to 10% FFA content) such as animal fats or crude palm oil. 99.9% of the co-solvent is recaptured and excess methanol used in the process is then recycled and reused [88].

The second approach utilizes methanol at very high temperature and pressure. This is known as supercritical methanol. The use of supercritical technology in the biodiesel production is an emerging technology. The supercritical methanol not only acts as a solvent but also as an acid catalyst [89]. The use of supercritical alcohol for the transesterification of neat vegetable oil is well-reported in literature [90–95]. However, its application in the transesterification of used cooking oil is not well documented in the literature.

As noted earlier, in the conventional transesterification of used cooking oil for biodiesel production, high free fatty acids and water always produce negative effects. To investigate the effect of water on the yield of methyl esters in transesterification of triglycerides and methyl esterification of fatty acids, Kusdiana and Saka [93] treated the triglycerides by catalyst-free supercritical methanol. The set reaction conditions were: molar ratio of methanol to oil, 42:1; supercritical treatment at 350 °C and 43 MPa, respectively. Results showed that the presence of water did not have a significant effect on the yield, as complete conversions were always achieved regardless of the water content. In fact, the presence of water at a certain amount could enhance the methyl esters formation. Also, it was observed that for the vegetable oil containing water, three types of reaction took place; transesterification and hydrolysis of triglycerides and methyl esterification of fatty acids proceeded simultaneously during the treatment to produce a high yield. When the results were compared with those methyl esters prepared by conventional methods, the finding showed that by a supercritical methanol approach, neat vegetable oil as well as its waste could be readily used for biodiesel production in a simple preparation. The results of this study are given in Table 8.

Reaction by supercritical methanol has some advantages [96,97]: (1) glycerides and free fatty acids are reacted with equivalent rates; (2) the homogeneous phase eliminates diffusive problems; (3) the process tolerates great percentages of water in the feedstock catalytic process which requires periodical removal of water in the feedstock or in intermediate stage to prevent catalyst deactivation; (4) the catalyst removal step is eliminated; and (5) if high methanol: oil ratio is used, total conversion of the oil can be achieved in a few minutes. Despite having all these advantages, the supercritical methanol method has some serious disadvantages. These include: (1) the process operates at very high pressures (25–40 MPa); (2) the high temperatures (350–400 °C) bring along proportionally high heating and cooling costs; (3) high methanol: oil ratios (usually set at 42:1) involve high costs for the evaporation of the un-reacted methanol; and (4) the process as posed to date does not explain how to reduce free glycerol to less 0.20% as established in international standards. Therefore, to apply this method on an industrial scale, further investigations of the production process, such as continuous operation and scale up, as well as economic evaluations, are needed.

A summary of the advantages and disadvantages of each technological possibility to produce biodiesel is presented in Table 9 [52].

3. Effect of reaction parameters on conversion yield of transesterification

The transesterification reaction involves some critical parameters which strongly influence the final yield. These parameters are not peculiar to transesterification of used cooking oil only but to triglycerides in general. From the review of the transesterification methods, the most relevant variables are:

- Free fatty acid and water content in the oil
- Reaction temperature

Table 8

Comparison of the yields of methyl esters in alkaline-catalyzed, acid-catalyzed and supercritical methanol.

Vegetable oil	FFA content ^a (wt%)	Water content (wt%)	Yield of methyl esters (wt%)		
			Alkaline-catalyzed	Acid-catalyzed	Supercritical methanol
Rapeseed oil	2.0	0.02	97.0	98.4	98.5
Palm oil	5.3	2.1	94.4	97.8	98.9
Used frying oil	5.6	0.2	94.1	97.8	96.9
Waste palm oil	>20.0	>61.0	No reaction	No reaction	95.8

^a Given as the weight percentage of free fatty acids, relative to vegetable oil

Table 9

Comparison of the different technologies of biodiesel production.

Variable	Alkali catalysis	Acid catalysis	Enzyme catalysis	Supercritical alcohol
Reaction temperature (°C)	60–70	55–80	30–40	239–385
Free fatty acid in raw materials	Saponified products	Esters	Methyl esters	Esters
Water in raw materials	Interference with reaction	Interference with reaction	No influence	
Yield of methyl esters	Normal	Normal	Higher	Good
Recovery of glycerol	Difficult	Difficult	Easy	
Purification of methyl esters	Repeated washing	Repeated washing	None	
Production cost of catalyst	Cheap	Cheap	Relatively expensive	Medium

- Molar ratio of alcohol to oil
- Type of catalyst
- Type/chemical structure of alcohol
- Amount/concentration of catalyst
- Reaction time
- Intensity of mixing (rpm)
- Use of co-solvents

4. Downstream processing of biodiesel

4.1. Separation of biodiesel

After the completion of the oil conversion reaction, biodiesel is a mixture of excess methanol, catalyst and glycerol. As a rule of thumb, difference in specific gravity of 0.1 in a mixture of compounds will result in phase separation by gravity. Gravity separation is suitable to recover biodiesel from the process byproducts (glycerol and alcohol). However, impurities in the feedstock may cause emulsion formation, which interferes with phase separation. Saturated salt (sodium chloride) or centrifugation breaks the emulsion and speeds up the phase separation [67].

Various devices and methods have been used in the separation of glycerol from biodiesel whether from virgin or used cooking oil. This section gives a summary of the methods and devices that have been applied in the separation of glycerol and biodiesel produced from UCO. Guo et al. [23] carried out the separation of crude ester from glycerol phase by decantation. Also, Felizardo et al. [19] separated glycerol rich-phase from methyl ester (biodiesel) layer in a decantation funnel. Azócar et al. [98] and Encinar et al. [11] utilized separation by sedimentation. Saifuddin and Chua [41] used microwave irradiation to carry out phase separation of glycerol and biodiesel. Wang et al. [69] used the process of centrifugation in the separation of glycerol from crude biodiesel. One of the most common devices used for separation of biodiesel from glycerol is separating funnel [14,76]. In separating glycerol from biodiesel, Issariyakul et al. [49] also used a separating funnel. Because of the peculiarity of the reaction, where glycerol was not separated by gravity from the ester phase, 1–2 g of pure glycerol was added to the reaction mixture and stirred for 15 min. The complete removal of glycerol was ensured by adding pure glycerol once for the upper layer and twice for the lower layer. Predojevic [50] used separating funnel and allowed the mixture to separate for 12 h. The glycerol was removed by gravity settling. Chhetri et al. [20], Phan and Phan [26] and Jordanov et al. [35], separated glycerol and crude biodiesel mixture into a separating funnel and the ester was separated by gravity.

4.2. Purification of biodiesel

This process is meant to remove impurities (those that can be removed) from biodiesel, after it is separated from the glycerol layer. These include alcohol, catalyst, entrained glycerol, soap, and other impurities.

4.2.1. Alcohol recovery

A good conversion reaction during transesterification will require excess alcohol, but the amount of alcohol in the system has to be minimized for good phase separation. The methods used in alcohol recovery are not peculiar to transesterification of UCO. However, the following methods have been used in recovery of alcohol after conversion of UCO to esters. One of the most popular methods is the removal of excess alcohol by evaporation. Lapuerta et al. [101] eliminated excess alcohol by evaporation. Alcantara et al. [17] eliminated excess methanol by evaporation under vacuum. Wang et al. [69] recovered excess methanol under vacuum (10 ± 1 mmHg) at 50 °C with a rotational evaporator. Dias et al. [37] recovered excess methanol from each phase (biodiesel and glycerol) separately, using a rotary evaporator under reduced pressure. Guo et al. [23] and Leung and Guo [36] removed excess methanol by evaporation under atmospheric condition. In using the method of evaporation, Predojevic [50] transferred crude ester into a sample flask of a rotary evaporator to remove methanol at 65 °C and 20 kPa. Issariyakul et al. [49] eliminated un-reacted alcohol using rotavapor at ~90 °C for 1.5 h.

Another method which has been used in alcohol recovery is distillation [51]. Arquiza et al. [18] carried out atmospheric batch distillation of methyl esters and collected distillates based on different temperature range. The distillate obtained at the lowest temperature range was determined to be methanol, showing that distillation allows for the recovery of the excess methanol used in transesterification reaction. Encinar et al. [11] subjected ethyl esters to distillation at 80 °C under a moderate vacuum (absolute pressure of 150 mmHg) to recover excess of ethanol.

To recover excess alcohol, crude esters phase has been washed several times with distilled water at various temperatures in a separating funnel, until the washings were neutral [25,26,76].

4.2.2. Washing of biodiesel

Washing provides valuable insight into the quality and completeness of transesterification—any soap, un-reacted oil, and unused catalyst present will make themselves known (if water is used, the wash water will be extremely soapy or the biodiesel and water will become suspended together in an emulsion). Washing methods include:

- Mist washing – in this method, water is finely misted (as with a spray bottle) onto the surface of the biodiesel, and because water is denser than biodiesel, water falls through the biodiesel picking up the soluble impurities along the way. The soapy, white, impurity-laden water gathers at the bottom of the wash container. Water is misted through it until it emerges clear, indicating that all soluble impurities have been removed from the biodiesel. The process is slow and it uses a lot of water, and usually the water is not re-used.
- Bubble washing – in this method, water is gently added to the biodiesel, one part water to two-part biodiesel, so there are two distinct layers. A bubbling mechanism, like an aquarium air-stone, is placed at the bottom of the container to produce very fine air bubbles. Because these bubbles start in the water layer,

water still encases the air upon reaching and passing through the biodiesel. Here, as with the mist method, small amounts of water interact with the biodiesel, drawing out soluble impurities. Upon reaching the surface of the biodiesel, the bubble bursts, and the water falls, passing through the biodiesel layer once more. Once this water is impurity-saturated, it can no longer extract any more from the biodiesel. So, either the used water is replaced by fresh water, or the biodiesel is moved to a new container for the second wash. Commonly, three washes are sufficient – the last of which does little except ensure that no impurities are left (water ought to be very clear) [100].

The advantages of bubble washing are: it is easy and does not take much effort. For added convenience a timer may be added to switch off the air-pump and when it is settled, the water is changed. The disadvantages of bubble-washing: it might not take much effort but it takes a lot of time. Bubble washing is gentle and can mask an incomplete reaction, which agitation will reveal immediately. A more complicated problem of bubble washing is biodiesel oxidation and polymerization.

Both methods (mist and bubble washing) are suitable for biodiesel produced by complete reaction.

- **Stir or mix washing** – in this method, 50% water and 50% biodiesel is used. Water is poured first and then biodiesel. A mixing device is used to stir the water/biodiesel mixture to the point of appearing homogeneous for several minutes. Since biodiesel has a lower specific gravity than water, the water will eventually separate and settle to the bottom and the biodiesel will remain on the top of water. As the mix settles out, the water will slowly sink, taking with it any soluble material. The top layer of biodiesel is siphoned off.

Advantages of stir-washing: The method is quick and effective, no masking of a poor reaction and there is no oxidation.

Biodiesel washing methods have also been classified into wet and dry washing. In wet washing, a fine water mist is sprayed over the biodiesel and as the water settles to the base of the wash container, the impurities are collectively removed. Dry washing methods allow for a strong affinity for polar compounds. Dry washing eliminates the need for wet washing as it reduces fresh water usage, disposal costs and significantly reduces overall operating cost.

In this review, washing with water was the mostly used in the production of biodiesel from UCO. Guo et al. [23], Reefat et al. [25] and Leung and Guo [36] washed crude ester phase with warm de-ionized water at 50 °C several times while Lertsathapornasuk et al. [43] washed ester twice with half a volume each of de-ionized water. Crude ester layer was washed with hot water until washings were neutral [14,26,49,69]. Al-Widyan and Al-Shyoukh [63] and Utlu and Koçak [100] reported washing biodiesel using pure water until the washing water was neutral. Chhteri et al. [20] and Saifuddin and Chua [41] used mist washing by spraying water onto the top of the cylinder containing the biodiesel at a low velocity. As part of the purification process, Encinar et al. [11] washed ethyl esters with distilled water. The same was used at 50 °C to wash crude ester phase three times until the washings were neutral [76]. Wang et al. [69] washed crude biodiesel with 10 wt% of water at 80 °C to remove soap.

To ensure high-quality fuel, several other methods have been used. To determine the influence of purification step on the methyl ester properties and yields, Predojevic [50] carried out the washing in a bed of silica gel (3 g, 2 cm internal diameter by 2 cm height); washing up to 7 times with 50 cm³ of 5%–phosphoric acid water solution until reaching the neutral pH and washing the crude methyl ester up to 10 times with 50 cm³ of hot distilled water at

50 °C until neutral pH. Acidulated water has been used by other researchers [99]. Felizardo et al. [19] washed methyl ester with water, then used 0.5% HCl solution and again with water. Biodiesel phase was washed first with 50% (v/v) of 0.2% HCl solution and after repeatedly with 50% (v/v) of distilled water until the pH of the washing water was the same as the distilled water.

4.2.3. Drying of biodiesel

When biodiesel fuel is clear, it is not colorless but translucent, one can see through it, there is no haze or cloudiness and then it is dry. Two methods are generally used in drying biodiesel: heating and use of chemicals.

Drying biodiesel requires little more than heating up the final biodiesel to 55 °C and holding it there for 15–20 min. Any remaining water should evaporate out or drop out easily where it can be drained out. Drying has also been carried out by heating the fuel approximately to 110 °C in an open container until there is no more steam from the fuel [9,11,101]. One advantage of heating is that it drives off any traces of remaining alcohol.

In the production of biodiesel from UCO, anhydrous sodium sulfate has been the most widely used chemical [14,23,25,26,36,37,41–43,50,74]. Other chemicals such as anhydrous magnesium sulfate have been used as well [19,76].

Wet crude biodiesel produced from UCO has been reported to be dried under vacuum (5 ± 1 mmHg) at 90 °C with a rotational evaporator for an hour [69].

4.2.4. Distillation of biodiesel

In order to obtain a final biodiesel product adhering to specifications, distillation has been used as the final purification step for biodiesel produced by UCO. When the high acid value such as found in UCO is used as the reactant, it is common to introduce distillation for the final purification of biodiesel to remove the impurities and unpleasant odor [102]. In some countries of EU where biodiesel fuel is used as a fuel without blended with fossil fuel, the crude biodiesel is distilled as the final product before use.

Arquiza et al. [18] carried out the separation of methyl esters obtained from used coconut oil by atmospheric batch distillation. The distillates collected were divided into four groups based on their temperature range: 63–64 °C (D1); 65–249 °C (T); 250–265 °C (D2) and 266–272 °C (FD). It was observed that the distillates were clear and colorless, indicating that the colored impurities did not volatilize up to a distillate temperature of 272 °C. Fraction D1 was determined to be methanol. The compositions of the feed (methyl esters from used frying oil), T, D2, and FD were determined by gas chromatography as shown in Table 10. Analysis showed that the bottoms left after distillation contains mostly methyl palmitate and methyl stearate which can be used as a diesel fuel substitute [103] or as lubricant additive for small diesel engines [104].

Wang et al. [70] carried out the distillation of FAME produced by transesterification of UCO using ferric sulfate. The distillations were performed in a 500 ml round bottom, one neck flask. The equipment includes a temperature controller, a receiver flask connected to a vacuum gauge and a condenser. A pump connected to the condenser provided vacuum. The dried crude biodiesel was

Table 10
Molar compositions of the distillates of methyl esters from UCO.

Component	Molar composition		
	Transition (T)	Second distillation (D2)	Final distillate (FD)
Methyl caprate	50.71	5.93	3.09
Methyl laurate	46.48	80.42	52.17
Methyl myristate	2.81	11.74	38.27
Methyl palmitate		1.91	6.48

fed to the flask, and the vacuum was adjusted to 40 ± 5 mmHg. The first distillate of the biodiesel was collected at 180°C . The distillate was terminated when no more FAME came out at the temperature 240°C (40 ± 5 mmHg), 93.0% of the biodiesel obtained.

Because distillation of biodiesel in both cases was a batch process, the double bond of unsaturated FAME would be dimerized as the residue of the distillation under high temperature ($\geq 200^\circ\text{C}$) and long time (>0.5 h). Distillation of biodiesel under the lower vacuum to decrease the distillation temperature or by wipe evaporator with continuous distillation should minimize the dimerization of the unsaturated FAME and improve the output. Zhang et al. [51] designed a process for fatty acid methyl esters distillation with different theoretical stages and reflux ratios. The system operated under vacuum to keep temperatures low enough to prevent degradation of the FAME.

5. Quality analysis of biodiesel

Various analytical methods have been developed for analyzing mixtures containing fatty acid esters and mono-, di-, and triglycerides obtained by transesterification of virgin and used cooking oils. Analyses have been performed by thin layer chromatography/flame ionization detector (TLC/FID), gas chromatography (GC), high performance liquid chromatography (HPLC), gel permeation chromatography (GPC), proton nuclear magnetic resonance (^1H NMR) and near infra-red spectroscopy (NIR).

In analyzing biodiesel from UCO, the preferred choice by most of the researchers' workers reviewed has been the use of gas chromatography. Most reports on the use of GC for biodiesel analysis employ flame-ionization detectors (FID), although the use of mass spectrometric detector (MSD) was employed in some cases to eliminate any ambiguities about the nature of the eluting materials since mass spectra unique to individual compounds would be obtained [105].

5.1. Thin layer chromatography method

Tomasevic and Siler-Marinkovic [14] reported the use of thin layer chromatography performed on glass plates coated with silica gel for the analysis of the methyl ester quality produced from used sunflower oil. The developing solvent used was petroleum ether, diethyl ether and acetic acid. Iodine vapor was used for visualization. The TLC showed the fuel contained only small amounts of mono- and diglycerides. In studying the effect of reaction time on transesterification, Leung and Guo [36] carried out the analysis of the product composition at different times for transesterification of Canola oil using thin layer chromatography. The results analyzed for neat Canola oil were observed to be similar for the used cooking oil, see Fig. 10 [36].

5.2. Gas chromatography method

Gas chromatographic method has been widely-used for the simultaneous determination of glycerol, mono-, di-, and triglycerides in vegetable oil methyl and ethyl esters. Literature is replete with information on the use of GC in the analysis of biodiesel produced from UCO. The compositions of methyl and ethyl esters from used frying oil have been determined by gas chromatography [17,18,23,26,50]. Several other researchers have used GC equipped with FID and different types of column packing and carrier gases have been used. Nitrogen has been used as carrier gas by [41,69–70,76,98], helium has been used by [19,20,25] while Lertsathapornasuk et al. [40,42] used hexane. On the other hand, Issariyakul et al. [49] reported the identification of fatty acid components of ester prepared from UCO using gas chromatography with mass spectrometric detector (MSD).

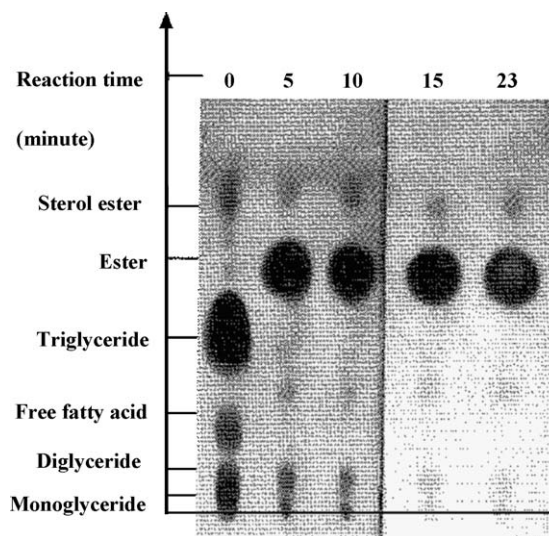


Fig. 10. TLC results of product composition at different reaction times for transesterified Canola oil.

5.3. High performance liquid chromatography method

The percentage yield of ethyl esters obtained from used vegetable oil has been quantified by HPLC on a silica column using hexane:diethyl ether:acetic acid (90:10:0.5 v/v) as mobile phase [40,42,43]. Similarly, HPLC has been used by Issariyakul et al. [49] to measure the percentage of purified ester in crude biodiesel. Tetrahydrofuran was used as a mobile phase.

5.4. Gel permeation chromatography method

Recently, Jacobson et al. [72] reported the analysis of biodiesel using gel permeation chromatography (GPC) equipped with a RI detector. THF was used as a mobile phase and the mono-, di-, and tri-glycerides, and methyl esters in the product were quantified by comparing the peak areas of their corresponding standards.

5.5. Thermo-gravimetric analysis method

Instead of the usual chromatographic analysis, Çayh and Küsefoğlu [34] carried out the determination of ester yields from UCO by thermo-gravimetric analysis (TGA). It was concluded that the TGA instrument, which gave the same results as chromatographic techniques, can be used to determine the yield of alkyl esters instead of GC or any other chromatographic method. Additionally, by using TGA one can measure the T^{50} ($^\circ\text{C}$) which is the temperature at which 50% of the material boils which can in turn be used to determine the cetane number of biodiesel. The TGA graphs are shown in Fig. 11 [34].

6. Fuel properties of biodiesel from used cooking oil

During frying, vegetable oil undergoes various physical and chemical changes, and some undesirable and unknown compounds are formed. Some of these compounds are polymers which are cleaved, and during the transesterification reaction, they form monomeric and dimeric fatty acid esters. The oligomeric compounds formed during frying increase the molecular mass and reduce the volatility of the oil. Therefore, the fatty acid esters obtained from frying oils influence the fuel characteristics (such as increasing the viscosity and reducing the burning characteristics), leading to a greater amount of Conradson Carbon Residue [15].

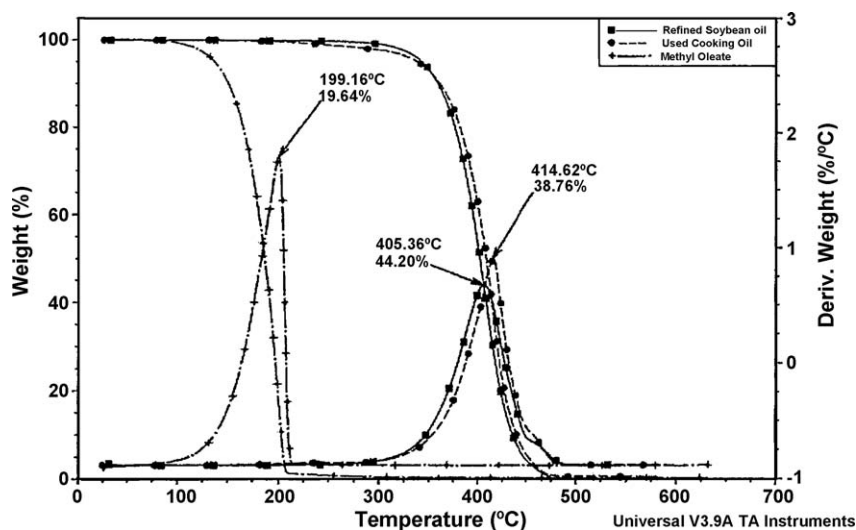


Fig. 11. TGA and derivative TGA graphs of methyl oleate, soybean oil and used cooking oil.

Table 11

Major parameters of the quality of biodiesel.

Parameters	Australia fuel standard (biodiesel) determination	Austria (ON C1191)	Czech Republic (CSN 6507)	France (journal official)	Germany (DIN 51606)	Italy (UNI 10635)	Sweden (SS 155435)	USA (ASTM D-6751)
Density at 15 °C (g/cm ³)	0.86–0.89	0.85–0.89	0.87–0.89	0.87–0.89	0.86–0.86	0.86–0.90	0.87–0.90	–
Viscosity at 40 °C (mm ² /s)	3.5–5.0	3.5–5.0	3.5–5.0	3.5–5.0	3.5–5.0	3.5–5.0	3.5–5.0	1.9–6.0
Flash point (°C)	120	100	110	100	110	100	100	130
CFPP (°C)	–	0/–5	–5	–	0–10/–20	–	–5	–
Pour point (°C)	–	–	–	–10	–	0/–5	–	–
Cetane number	51	≥49	≥48	≥49	≥49	–	≥48	≥47
Neutralization number (mg KOH/g)	≤0.8	≤0.8	≤0.5	≤0.5	≤0.5	≤0.5	≤0.6	≤0.8
Conradson carbon residue (%)	0.05	0.05	0.05	–	0.05	–	–	0.05

Since the properties of biodiesel fuel produced vary with its production feedstock, those countries that have adopted biodiesel stipulate their own specifications for biodiesel. These properties play a vital role in quality control in the petroleum-based fuel industry. The parameters which define the quality of biodiesel can be divided into two groups. One group contains major parameters, which are also used for mineral oil-based fuel, and the other group especially describes the chemical composition and purity of fatty acid alkyl esters [4,106]. Table 11 shows the specifications of major parameters of biodiesel in some countries and Table 12 contains the vegetable oil specific parameters and the corresponding value of fatty acid methyl esters according to standards of the countries in the table.

Density is an important property mainly in airless combustion systems because it influences the efficiency of atomization [19]. It is known that biodiesel density mainly depends on its alkyl esters

content and the remained quantity of alcohol [11,50]; hence this property is influenced primarily by the choice of vegetable oil [106]. For comparison, the density values between 850 and 900 kg/m³ are adopted by many national standards.

It has been noted that during frying, oxidation and polymerization of triglycerides take place thereby raising the viscosity of used frying oil. Hence, the extent of the transesterification reaction, as well as the experimental conditions used in biodiesel production, greatly influences the viscosity [19]. Different viscosities are due to the incomplete reaction of the UCO or to the inherent biodiesel purification, leaving conjugated or free glycerol in the alkyl ester phase. In fact, the presence of glycerides changes the apparent viscosity of alkyl esters, revealing the extent of the transesterification reaction and the alkyl esters phase purity [107]. Among the major parameters for biodiesel, the viscosity controls the characteristics of the injection from the diesel injector. High

Table 12

Vegetable oil specific parameters for the quality of biodiesel.

Parameters	Australia fuel standard (biodiesel) determination	Austria (ON C1191)	Czech Republic (CSN 6507)	France (journal official)	Germany (DIN 51606)	Italy (UNI 10635)	Sweden (SS 155435)	USA (ASTM D-6751)
Methanol/ethanol (%mass)	0.2	≤0.2	–	≤0.1	≤0.3	≤0.2	≤0.2	–
Ester content (%mass)	≥96.5	–	–	≥96.5	–	≥98	≥98	–
Monoglyceride (%mass)	–	–	–	≤0.8	≤0.8	≤0.8	≤0.8	–
Diglyceride (%mass)	–	–	–	≤0.2	≤0.4	≤0.2	≤0.1	–
Triglyceride (%mass)	–	–	–	≤0.2	≤0.4	≤0.1	≤0.1	–
Free glycerol (%mass)	≤0.02	≤0.02	≤0.02	≤0.02	≤0.02	≤0.05	≤0.02	≤0.02
Total glycerol (%mass)	≤0.25	≤0.24	≤0.24	≤0.25	≤0.25	–	–	≤0.24
Iodine number	–	≤120	–	≤115	≤115	–	≤125	–

values of viscosity give rise to poor fuel atomization, incomplete combustion, and carbon deposition on the injector. Therefore, the biodiesel viscosity must be low. The value required by all the standards (see Table 12), at 40 °C, must not be greater than 6 mm²/s.

Flash Point is a parameter to consider in the handling, storage, and safety of fuels and flammable materials. High values of flash point decrease the risk of fire which is safe for transport purpose, and this circumstance represents an advantage of biodiesel in relation to petro-diesel. The various standards specify flash point above 100 °C.

Cold filter plugging point reflects the cold weather performance of a fuel. At low operating temperature fuel may thicken and might not flow properly affecting the performance of fuel lines, fuel pumps and injectors. Similar to CFPP is the cloud point and pour point respectively. Both parameters are often used to specify cold temperature usability of fuel oils [108]. These parameters follow a parallel evolution with CFPP. However, CFPP defines the fuel's limit of filterability, having a better correlation than cloud point for biodiesel as well as petroleum diesel. Normally either pour point or CFPP are specified. In general, the values of CFPP, cloud point and pour point of biodiesel from UFO are high (in comparison with mineral diesel) due to the presence of some unknown compounds and the formation of polymerized esters during transesterification. Hence biodiesel from UFO would be a suitable candidate as a diesel fuel substitute in tropical climates and during the summer and can be used only during the winter by the application of suitable additives [11,49].

Cetane number is an indicator of the quality of fuel. It measures how easily ignition occurs and the smoothness of combustion. The higher the cetane number, the better is the ignition properties. Cetane number affects engine performance characteristics like combustion, stability, noise, drive-ability, white smoke, and carbon monoxide and hydrocarbon emission. Biodiesel has higher cetane number than mineral diesel, which results in higher combustion efficiency. This has been explained by the oxygenated nature of biodiesel fuel [8]. The various national standards specify cetane number greater than 47.

Heating value is another important property of ester fuel as it is aimed for use as a diesel fuel substitute. It has been noted that calorific value of esters are not much different from their parent oil waste fryer grease [49]. Therefore, there are no standard specifications about the calorific value of biodiesel. Generally, it has been reported that biodiesel contains approximately 10% less energy when compared to petroleum-based diesel. This indicates that approximately 10 vol% more biodiesel would be required compared to petroleum diesel fuel for the travel of the same distance [8,11,49]. The lower value is due to the presence of oxygen in biodiesel [26].

Carbon residue is an indicative of carbon depositing tendencies of a fuel. It is an important indicator to measure the tendency to form carbonaceous deposits in engines, which can cause several operational problems such as blockage of nozzles, corrosion, cracking of components. Conradson carbon residue (CCR) for biodiesel is more important than that in mineral diesel fuel because it shows a high correlation with presence of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids and inorganic impurities [109]. Phan and Phan [26] have reported that carbon residue content increases exponentially with percentage of biodiesel when blended with mineral diesel. According to the report, the level of carbon residue content at a percentage of the biodiesel above 20 vol% exceeded the current biodiesel specification of 0.3 wt% (at 10% distillation remnant) or 0.05 wt% (at 50% distillation). This is one of the disadvantages of biodiesel in considering it a substitute fuel for engines. The report concluded that it was vital to have major modifications in engines fuelled with 100% biodiesel in order to overcome the operational problems mentioned earlier.

The acid value measures the content of free fatty acids in the fuel sample. This property is specified to ensure proper ageing of the fuel and/or a good manufacturing process. Various standards have fixed the value of this parameter in the range of 0.5–0.8 mg KOH/g.

Iodine value allows determination of the degree of un-saturation of biodiesel fuel. This property greatly influences fuel oxidation and the type of aging products, and deposits formed in diesel engine injectors. Issariyakul et al. [49] have reported that the type of parent oil used is the major parameter affecting the iodine value. During the frying process, oil is continuously or repeatedly subjected to high temperatures in the presence of air and moisture. Under these conditions, a variety of degradation reactions occur, such as auto-oxidation, thermal polymerization, thermal oxidation, isomer cyclization and hydrolysis [12,15,34,46]. These reactions normally raise the iodine value of UFO; hence several samples of biodiesel reveal iodine values close to those of the UFO [19,49,50].

The presence of high level of alcohol in biodiesel cause accelerated deterioration of natural rubber seals and gaskets. Methanol contaminates methyl ester phase and is responsible for metal corrosion, particularly of aluminum, and for the decreasing of the fuel flash point [19]. Therefore, control of alcohol content is required.

Biodiesel fuel consists mainly of fatty acid alkyl esters and its quantities are specified according to the specifications of various countries. The presence of mono-, di- and tri-glycerides cause engine problems like fuel filter plugging affecting the fuel properties and are specified in most biodiesel standards.

Table 13

Some properties of biodiesel produced from selected UCO compared with petroleum diesel fuel.

Property	Biodiesel							Typical diesel	
	WFOME ^a	WFOME	Waste palm oil	WME ^b /WEE ^c	WFPO ^d	WCOM ^e /WCOE ^f	UCO	UVOEE ^g	
Density at 15 °C (kg/m ³)	890	888	873.7	888.2/854.8	877.2–	887/878	–	887.2	845
Kinematic viscosity at 40 °C (mm ² /s)	4.23	4.32	–	4.68/4.98	6.32	5.16/4.92	5.18	6.13	3.47
Heating value (MJ/kg)	–	39.55	39.31	37.27/40.72	39.87	39.26/39.48	–	–	45
Cetane number	54.5	52.0	–	–	62	–	48	47.9	50
Flash point (°C)	171	156	109	–	130	–	148	130	>52
Pour point (°C)	–	–2.5	0	–3/–6	10	–	–4	10	<10
Cloud point (°C)	–	3	0	1/–2	–	–	–	10.7	–5
CFPP (°C)	1	–	–	–6/–4	–	–	–	–	–

^a Waste frying oil methyl ester.

^b Waste fryer grease methyl ester.

^c Waste fryer grease ethyl ester.

^d Waste frying palm oil.

^e Waste cooking oil methyl ester.

^f Waste cooking oil ethyl ester.

^g Used vegetable oil ethyl ester.

Some properties of biodiesel fuel produced from UCO [42,43,49,63,76,99,101,111] compared with petroleum diesel are shown in Table 13.

7. Economic feasibility

The economic feasibility of biodiesel depends on the price of crude oil and the cost of transporting diesel long distances to remote markets [8]. It is certain that the cost of crude oil is bound to increase due to increase in its demand and limited supply. Further, the strict regulations on the aromatics and sulfur contents in the diesel will result in higher cost of production of diesel fuels. The cost of producing methyl or ethyl esters from edible oil is currently much more expensive than hydrocarbon-based diesel fuel.

The cost of biodiesel can be reduced if UCO considered instead of neat, edible oil. With the mushrooming of fast food centers and restaurants in the world, considerable amounts of UCO are discarded. These oils are now used for making biodiesel, thus helping to reduce the cost of water treatment in the sewage system and in the recycling resources.

Though the use of UCO in making biodiesel has helped to reduce the cost of biodiesel, yet biodiesel is not economically feasible, and more research and technological development will be needed [110].

8. Conclusions

Biodiesel as an alternate fuel for diesel engines has become increasingly important due to environmental consequences of petroleum-fuelled diesel engines and the decreasing petroleum resource. The main challenges are its cost and availability of fats and oils resources. By collecting used frying oils and converting them to biodiesel fuel, the cost of biodiesel is significantly lowered and the negative impact of disposing used oil to environment reduced. However, in the process of frying, oil undergoes many reactions leading to the formation of many undesirable compounds such as polymers, free fatty acids, and many other chemicals. This poses a lot of challenges in the transesterification of UCO. The pretreatment of the UCO to remove these chemicals is not practical; hence the oil is heated and filtered to remove solid particles prior to transesterification.

The following types of transesterification are possible: alkali-catalyzed transesterification, acid-catalyzed transesterification, acid- and alkali-catalyzed two-step transesterification, enzyme-catalyzed transesterification and non-catalytic conversion technique for transesterification. The type of transesterification selected is dependent on the FFA and water contents. If the FFA and water contents are <1 wt% and <0.5 wt%, respectively, then an alkaline catalyst is more suitable. As per the reported literatures, NaOH, KOH and NaOCH₃ are the most widely used alkaline catalysts with KOH commonly used for producing biodiesel from waste recycled oil feedstock. To reduce the reaction time and separation time, microwave irradiation technique has been used in alkaline transesterification. However, improper control of the reaction time may lead to deterioration of both biodiesel yield and purity.

If the FFA content of oil is >1 wt%, then an acid catalyst is a good choice. However, this process requires high catalyst concentration and high molar ratio leading to corrosion problems. The most commonly used acids are sulfuric and sulfonic acids. Despite its operation under high pressure and temperature, the use of solid acids could be a better choice for the transesterification of UCO with high FFA.

The advantages of both methods have been combined in the two-step transesterification reaction. However, it requires many steps which may increase production cost. In the conventional

transesterification reaction, both methanol and ethanol can be used as esterifying agents, methanol being the most widely used. There are very few studies reported on the use of other alcohols. For the alkyl-catalyzed reaction, it was found that it is a very good process of production of biodiesel from UCO with relatively high conversion.

The use of enzymes is a great viable method to all chemical-catalyzed reactions for the production of biodiesel from UCO.

In the case where supercritical alcohol was used, higher rates of reaction were observed when compared to conventional transesterification. Another advantage of this process is that the FFAs are converted completely into esters. However, the requirements of high temperature, high pressure and high molar ratio of oil to alcohol make the process costly for industrial scale.

The quality of biodiesel is most important for engine parts. Hence various downstream processing: separation of biodiesel from glycerol, purification to remove/recover alcohol, biodiesel washing, drying and where specified, distillation are carried out.

To check the quality of biodiesel produced, various standards have been specified. As per the analytical methods reported in literature, chromatographic methods have been widely used. However, a new method of TGA has been used which has an added advantage of measuring the T^{50} (°C) which is the temperature at which 50% of the material boils which can in turn be used to determine the cetane number of biodiesel.

The biodiesel was characterized by determining the density, viscosity, calorific value, cetane number, flash point, cloud and pour points. The characteristic properties of biodiesel are same as that produced from virgin oils and are generally similar to those of petroleum diesel fuel. The fuel properties of biodiesel derived from UCO, all met the various national biodiesel standards. Thus, biodiesel produced from UCO can be used in diesel engines without any engine modifications.

Acknowledgements

The financial assistance of Tshwane University of Technology, Pretoria towards this research is hereby acknowledged. Opinions expressed and conclusions arrived at, are those of the authors and are not necessarily to be attributed to the Tshwane University of Technology.

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